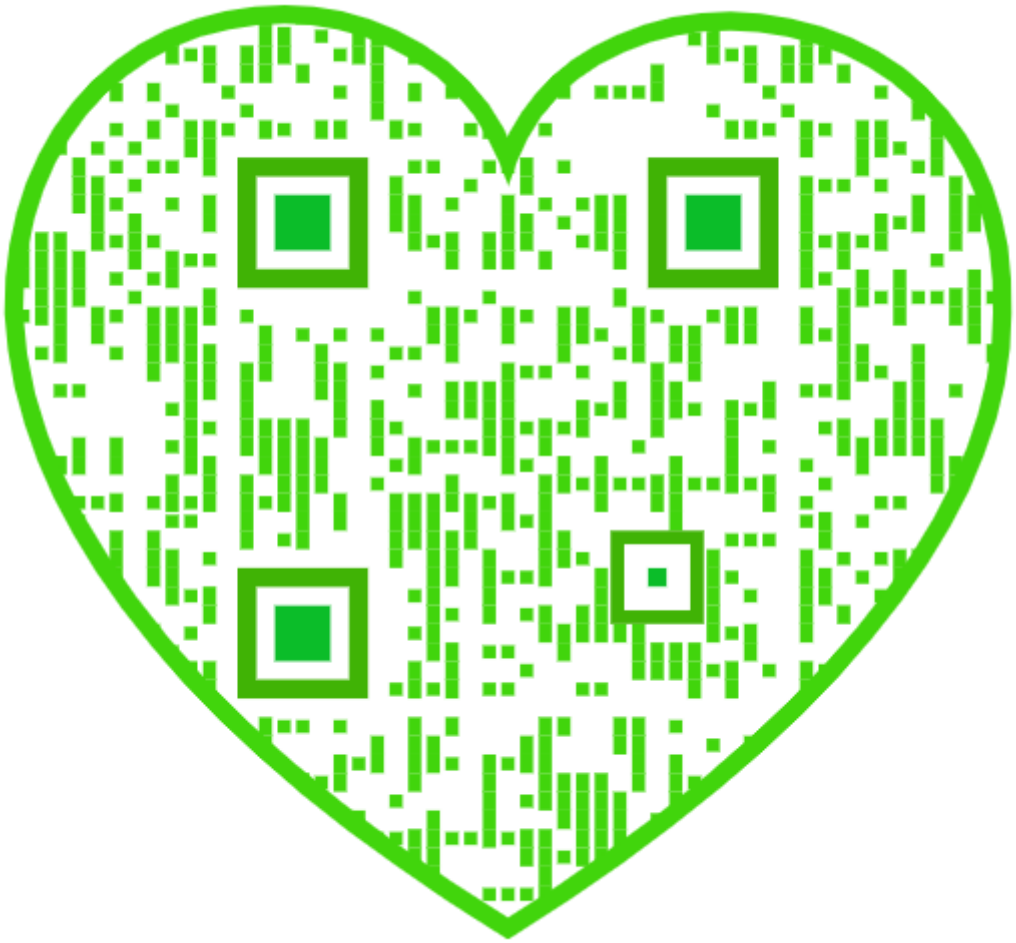
UNIVERSITY OF TORONTO
3 1761 01186660 5



THE MANUFACTURE OF LEATHER

Ben

THE MANUFACTURE OF LEATHER

BY

HUGH GARNER BENNETT., M.Sc., F.C.S

MEMBER OF THE INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS; ASSISTANT LECTURER AND DEMONSTRATOR AT THE LEATHER INDUSTRIES DEPARTMENT OF THE UNIVERSITY OF LEEDS

FOURTH IMPRESSION

163506
9/8/21

LONDON

CONSTABLE & COMPANY LTD.

10 ORANGE STREET LEICESTER SQUARE W.C.

1920

Printed in Great Britain

PREFACE

The manufacture of leather is now a chemical industry, and in this volume it has been the author's aim to treat it as such. The book is written for the general student of this branch of chemical technology, and an attempt has therefore been made on the one hand to keep the phraseology from being too scientific, in order that it may be intelligible to the intelligent workman, and on the other hand to keep it from being too technical in order that it may be of use to the pure chemist who wishes to apply his knowledge in the leather industry.

On the technical side the author has endeavoured in his descriptions of practical methods to give prominence to those processes which are at present most widely used, but as the details of these processes vary so very much in different parts of the country and change so rapidly under the march of modern progress, it has been considered useless to enter into a minute description of them. At the most they may be taken as to some extent typical of what is employed in this country, and in no case is it claimed that the methods described will produce the best possible results. This is particularly true with regard to the finishing processes that are given. The reader who scans the later chapters of this book in the hope of discovering new and wonderful recipes for "seasons," "finishes," etc., will search in vain. For the most part the recipes mentioned in the text are old and well known, and have been selected by the author merely from the standpoint of what was typical.

On the scientific side it has been necessary to assume that the reader has some acquaintance with chemistry and with the common analytical methods; hence if any obscurity is encountered, reference should be made to the standard text-books. Only those analytical processes have been given which are suitable for works control, and which in the author's

experience have been found to combine tolerable accuracy with rapidity of manipulation, regard being paid also to the convenience and probable resources of the works chemist.

Some attempt has also been made to meet the needs of the candidates for the examinations of the City and Guilds of London Institute, and for the Degree and Diploma examinations of the Leather students of the Leeds University.

The author wishes to acknowledge his indebtedness to many kind friends for assistance in preparation of this book. For illustrations of leather-working machinery the author it indebted to Messrs. T. Haley & Co., Messrs. Farrar and Young, Messrs. Huxham and Browns, Messrs. The Turner Co. Ltd., Messrs. The Mœnus Machine Works, Ltd., Messrs. E. Wilson & Son, and Messrs. The Mirrlees Watson Co., Ltd. The author's thanks are also due to Messrs. West, Newman and Co. for the loan of their block of the warble fly, to Messrs. E. J. Richardson, of Newcastle, and Messrs. Walker, Ltd., of Litherland for the illustrations representing work in their factories, and to Mr. H. Brumwell and Mr. C. H. Crabtree for their assistance in preparing other illustrations. In proof revision the author has received invaluable assistance from Prof. H. R. Procter, and desires to acknowledge here his kindness and helpful criticism.

CONTENTS

CHAPTER I

Historical and Introductory Outline

	PAGE
Origin of leather manufacture	1
Historical development of different tannages	2
The changes of this last century	3
Brief outline of chief manufacturing processes	4—5

CHAPTER II

The Nature of Skin

Its physical structure	6
Nature of epidermis	6
Growth of hair	7
Nature of corium or true skin	8
Microscopic examination of skin structure	9
Its chemical composition	10
General properties of proteids	11
Gelatin and its decomposition	16

CHAPTER III

Fermentation

Simplest forms of life	19
Organised and unorganised ferments	20
Yeasts	21
Moulds and bacteria	22
Putrefaction	24
Fermentations in leather manufacture	25

CHAPTER IV

Hides and Skins

	PAGE
Curing hides by drying	27
,, ,, salting	28
,, ,, dry salting	29
Criteria for selection of hides	29
Warbles	30
Sources of supply of hides	33
E. I. kips	36
Sheep skins	36
Goat skins	39
Seal skins	40

CHAPTER V

Water

Nature of hardness	41
Softening by Clark process	42
,, ,, Porter-Clark process	42
,, ,, Archbutt and Deeley process	43
,, ,, caustic soda process	43
Water analysis	44
Suitability of waters for tanners' purposes	46

CHAPTER VI

Soaking

Nature of the process	49
Danger of bacterial action	50
Mechanical treatment in drums, stocks, etc.	50
Chemical assistance in soaking	52
Use of caustic soda and sodium sulphide	53
Practical treatment of market hides	54
Soaking salted hides	54
Dried hides and dry-salted hides	55
E. I. kips	55
Calf skins	55
Goat skins	55
Seal skins	56
Chemical control of soaking	56

CHAPTER VII

Unhairing

PAGE

Depilation by sweating 57
Cold-sweat system 57
Warm-sweat system 58
Depilation by lime 58
Mode of action of lime 61
Use of sodium sulphide as depilatant 62
„ arsenic sulphides in limes 63
„ caustic soda in limes 64
Bacterial action in limes 64
Action of ammonia 65
Principles of liming 65
The mechanical operations of the lime-yard: hauling, unhairing, fleshing, rounding, etc. 66
Unhairing machines 69
Fleshing machines 73
Systems of liming 74
Three-pit system 75
One-pit system 78
Pullman-Payne system 79
Suspension systems 80
Practical methods of liming 80
Hides for sole leather 80
Buffalo method 81
Quick processes 82
Hides for belting leather 83
„ harness leather 83
„ dressing leather 84
E. I. kips 84
Calf skins 84
Fellmongering sheep and lamb skins 85
Kid and lamb skins 88
Goat skins 89
Seal skins 90
Chemical control of lime-yard 90

CHAPTER VIII

Deliming

Principles of deliming 92
Puering 93
Bating 97

CHAPTER VIII.—*continued.*

PAGE
Drenching 98
Chemical deliming agents—boric acid, lactic acid, etc. . . . 100
Practical methods of deliming 102
Sole butts and offal 102
Strap butts 103
Harness backs 103
Dressing hides 104
E. I. kips 105
Calf skins 105
Sheep skins 107
Degreasing 107
Pickling 108
Defects in Sheep skins 110
Kid skins 111
Goat skins 111
Seal skins 112
Chemical control of deliming processes 112

CHAPTER IX

The Tannins

Definition and properties of tannins 113
Methods of purification of tannins 114
Classification 115
Pyrogallol tannins and associated substances 116
Gallic acid 116
Ellagic acid (bloom) 117
Gallotannic acid 117
Ellagitannic acid 119
Catechol tannins and associated substances 119
Catechins (whites) 120
Phlobaphenes (reds) 121
Catechutannic acid 121
Quercitannic acid 121
Quebrachotannic acid 121
Flavones 121

CHAPTER X

The Vegetable Tanning Materials

Sources of tannin in plants 123
Pyrogallol tanning materials 124
Valonia 124

CHAPTER X.—*continued*

PAGE

Myrobalans 126
Divi-divi 129
Algarobilla 129
Sumach 129
Pistacia 131
Oakwood extract 132
Chestnut extract 132
Willow bark 132
Knoppern 133
Turkish galls 133
Catechol tanning materials 133
Oak bark 133
Gambier 134
Quebracho and its extracts 135
Hemlock bark 136
Mangrove ,, ... 137
Mimosa ,, ... 137
Mallet ,, ... 138
Birch ,, ... 139
Larch ,, ... 139
Pine ,, ... 139
Canaigre 139
Cape sumach 139

CHAPTER XI

The Analysis of Tanning Materials

Löwenthal method for used liquors, spent tans, etc. . . . 140
Indirect gravimetric method 142
Sampling from bulk 142
Preparation of infusion 143
Extraction for analysis 144
Filtration 145
Detannisation 146
Filter bell method 147
Procter-Bennett shake method 148
Standardisation of hide powder 149
Evaporation and drying 149
Statement of results 150
I.A.L.T.C. official method 151
Measurement of colour by tintometer and by pelt test . . 154
Barkometer 155
Beaumé degrees 156

CHAPTER XII

The Preparation of the Tanning Liquors

PAGE
Grinding 157
Grinding mills 158
Disintegrators 158
Shredding mills 159
Leaching 160
Pumping system 161
Press leach system 162
Heating leach liquors 163
Extraction under pressure 164
Sprinkler leaches 164
Extract manufacture 164

CHAPTER XIII

The Principles of Vegetable Tanning

Chemical and physical actions both probably involved . . . 168
Gradual increase in strength of liquors 168
Astringent and mellow liquors 169
Free acid (sourness) in yard liquors 170
Suspenders 171
Paddles 171
Handlers—dusters and floaters 172
How a round of handlers may be worked 173
Working liquor packs and dusters 176
Layers 177
Principles of drum tanning 177

CHAPTER XIV

The Tannage of Sole Leather

The oak-bark tannage 179
The West of England tannage 181
The modern mixed tannage 183
Working the layers 185
Working the liquors 188
American sole leather 189
Union tannage 191
Drum tannages 192

CHAPTER XV

The Tannage of Belting, Harness and Upper Leather, Etc.

PAGE
Belting leather 194
Harness leather 195
Dressing hides for upper leather 197
Dressing leather liquors 199
Dressing hides for legging leather 200
E. I. kips 200
Calf skins for upper leather 201
Hides for bag, portmanteau and bridle work, etc. . . . 202
Picking band butts 203

CHAPTER XVI

The Tannage of Moroccos and Light Leathers

Goat skins for moroccos 204
Seal skins for moroccos 206
Calf skins for bookbinding and fancy work 207
Sheep skins for basils, skivers, roans and roller leather, etc. . . 208

CHAPTER XVII

The Tannage of Chrome Leather

Historical development 210
Nature of the mineral tannages 211
The two-bath process 213
The chroming bath and its modifications 213
The reducing bath 216
The reactions given by Eitner and Stiasny 217
The one-bath process 219
Principles of one-bath tannage 221
Mode of penetration of chrome salts 222
Basic chrome liquors 223
Chrome alum liquor 223
Glucose liquor 224
General qualities of chrome leather 225
The tannage of calfskins and hides for "box calf," etc. . . . 227
Goat skins for glacé 230
Sheep skins for imitation glacé 232
Chrome chamois 233
Picking band butts 234
Motor butts, strap butts, harness backs, sole butts, etc. . . . 235
Analytical control of the chrome tannages 236

CHAPTER XVIII

Alum and Combination Tannages

PAGE
Principles of tawing 239
Combination tannages 240
Lamb and kid skins for glove kid 241
Calf skins for calf kid 242
Goat skins for dongola 243

CHAPTER XIX

Fat, Oil and Aldehyde Tannages

Fat tannages 245
Helvetia and Crown leathers 246
Chamois leather 247
Buff leather 248
Buck leather 249
Formaldehyde leather 250

CHAPTER XX

The Drying of Leather

Principles of drying 251
Wet and dry bulb thermometers 252
Weather drying 253
Screw fan ventilation 254
Centrifugal fan ventilation 255
Downward ventilation 255
Turret drying 255
Stove drying 256
Samming 256
Methods employed for heavy and light leathers 256

CHAPTER XXI

The Finishing of Sole Leather

Butts from a mixed tannage for "scoured bends" 259
Scouring 259
Vatting 261
Shedwork, oiling and drying 262
Striking out, pinning, etc. 263
Rolling "on" and "off" 263
Brushing 266
Drum scouring offal 267
Butts from a West of England tannage, for "bloomed butts" . 268
Butts from an oak bark tannage 269
American hemlock sides 269
Drum-tanned sole leather 271

CHAPTER XXII

The Currying and Finishing of Dressing Leather

PAGE

Nature of currying 274
Soaking 274
Shaving, by hand and machine 274
Splitting, by union, vibrating knife and band knife machines . . 277
Stoning or "jacking," skiving, etc. 281
Scouring, by hand and machine 282
Sumaching 285
Principles of stuffing 285
Hand stuffing 288
Drum stuffing 288
Burning in 292
Spueing of curried leathers 293
Currying and finishing strap butts 295
Black harness 297
Brown harness 300
Waxed kip butts 301
Waxed calf 303
Waxed splits 303
Waxed shoe butts 304
Army grains 304
Satin leather 304
Memel butts 306
Levant 307
Glove hide bellies 307
Lining leather 308
Bag hides 308
Bridle leather 308
Kip bellies for straps 310
Legging leathers 310
Picking band butts 310

CHAPTER XXIII

Leather Dyeing

Introduction of coal tar colours 312
Classification of artificial dyestuffs into basic and acid colours . 312
Basic colours 312
Acid colours 314
Commercial dyestuffs 316
The natural dyestuffs, logwood, etc. 317
Mordants 319

CHAPTER XXIII.—*continued.*

PAGE
Bleaching 320
Colour shades 321
Methods of dyeing 324
Tray method 324
Paddle method 327
Drum method 328
Brush dyeing or staining 329
Theory of dyeing 330

CHAPTER XXIV

The Finishing of Light Leathers

Preparation for dyeing,—stripping, souring, sumaching, striking out, etc. 332
Graining or boarding 336
Embossing and printing 338
Seasoning 340
Glazing 341
Fluffing 343
Goat skins for hard-grain moroccos 344
,, ,, levant, blacks and colours 345
Seal skin moroccos 346
Basils for linings, slipper, legging and gaiter leather . . . 348
Skivers for paste grain, straight grain, hat leathers, etc. . . 349
Roans 350
Roller leather 350
E. I. sheep and goat for moroccos, linings, roller leather, glacé, bronzed leather, etc. 351
Hide splits for common upholstery 354

CHAPTER XXV

The Finishing of Chrome Leather

Neutralisation 355
Fat-liquoring 356
Staking 358
Finishing box calf 360
Box calf imitations 361
Glacé calf, dull calf 362
Waterproof chrome upper leather 362
Willow calf 363
Glacé kid 364

CHAPTER XXV.—*continued.*

PAGE
Dull kid coloured glacé 365
Imitation glacé 366
Chrome chamois 367
Picking band butts 368
Harness backs 368
Strap, motor and sole butts 369

CHAPTER XXVI

The Finishing of the Alum- and Combination-tanned Leathers

Glove kid 371
Calf kid 373
Glazed dongola goat 373
Combination chrome glacé 374
Semichrome box and willow calf 375

CHAPTER XXVII

The Finishing of Fat and Oil-tanned Leathers

Helvetia and Crown leathers 376
Chamois for wash-leather 376
Chamois for gloving 376
Bleaching chamois 376
Dyeing chamois 378
Buff, buck and formaldehyde leathers 379

CHAPTER XXVIII

Japanned and Enamelled Leathers

Nature of japanning and enamelling 380
Preparatory processes 380
Manufacture of the japan 382
Application of the japan 383

CHAPTER XXIX

The Dressing of Wool Rugs

Principles of rug dressing with sheepskins 385
Dressing blacks 387
Dressing whites 391

CHAPTER XXIX.—*continued.*

PAGE

Dressing greys 391
„ browns 392
„ walnuts 393
„ crimsons 394
„ blues 395
„ greens 396
China sheep skins 396
Angora goat skins 396
Rabbit skins 396

CHAPTER XXX

The Analysis of Leather

Estimation of hide substance 397
„ „ moisture and fat 400
„ „ water soluble matter 401
„ „ glucose 402
Estimation of mineral ash 403
„ „ free mineral acid 404
Typical analyses 405

INDEX 409–420

LIST OF ILLUSTRATIONS

FIG.		PAGE
1.	Vertical section of calfskin.	7
2.	Structure of epidermis	8
3.	Cowhide, rough-tanned	9
4.	Cowhide, rolled	10
5.	Pigskin	11
6.	E. I. goatskin	12
7.	Calfskin	13
8.	Welsh sheepskin.	14
9.	Yeast cells.	21
10.	Mould (*Penicillium glaucum*)	22
11.	Bacteria	23
12.	Warble fly (*Hypoderma bovis*)	30
13.	Tail-weights	31
14.	Rounding a hide.	32
15.	Stocks	51
16.	Scotch tumbler	51
17.	Latticed drum	52
18.	Limeyard (Messrs. Walker, Ltd., Litherland)	60
19.	Unhairing by hand labour.	62
20.	Fleshing by hand labour	64
21.	Beamhouse tools	67
22.	Drum beamhouse machine.	68
23.	The Conus unhairing machine	69
24.	The Leidgen unhairing machine	70
25.	Whitney unhairing and fleshing machine	71
26.	Serial table unhairing machine	72
27.	The "Continua" fleshing, unhairing and setting out machine	73
28.	The "Cylindra" fleshing, slating, and setting out machine	74
29.	Wilson fleshing machine	75
30.	Rubber roll fleshing machine	76
31.	Scudding with a hand knife	93
32.	Puering paddle	94
33.	Smyrna and Greek valonia (*camata*)	125
34.	Myrobalans	127
35.	Sicilian sumach (*Rhus coriaria*)	129
35A.	Photo-micrographs of sumach, its adulterants and substitutes	*facing* 130

FIG.		PAGE
36.	American sumach (*Rhus glabra*).	131
37.	Common oak (*Quercus robur*)	133
38.	Hemlock firs (*Pinus canadensis*)	136
39.	Golden Wattle (*Acacia pycnantha*)	137
40.	Green Wattle (*Acacia dealbata*, variety of *A. mollissima*)	137
41.	Black Wattle (*Acacia binervata*)	138
42.	Students' laboratory, Leather Industries Department of the University of Leeds	141
43.	Procter extractor	144
44.	Filtration apparatus with Berkefeld candle (upward filtration).	146
45.	Filtration apparatus wit Berkefeld candle (downward filtration)	146
46.	Procter's filter-bell apparatus	147
47.	Shake machine for the Procter-Bennett method of tannin analysis	148
48.	Tintometer.	154
49.	Barkometer.	155
50.	Bark breaker	157
51.	Grinding mill	158
52.	Myrobalans husking machine	159
53.	Disintegrator	159
54.	Battery of press leaches	161
55.	Yaryan evaporator	165
56.	Tan yard (Messrs. Walker, Ltd., Litherland)	184
57.	Tanning drum	192
58.	Double paddle for light leather tanning	205
59.	Tanning paddle	226
60.	Screw fan	254
61.	Samming machine	257
62.	Wilson six-arm butt scourer	260
63.	Wilson butt striker	261
64.	Wilson's single-bed butt roller	264
65.	Wilson's twin-bed butt roller	265
66.	Brushing machine	266
67.	Priestman striker	267
68.	Offal roller	268
69.	Pendulum roller	270
70.	Portion of leather warehouse (Messrs. Walker, Ltd., Litherland)	271
71.	Loads of leather leaving tannery (Messrs. Walker, Ltd., Litherland)	272
72.	Hand-shaving	275
73.	Shaving machine	276
74.	Union splitting machine	278
75.	Band-knife splitting machine	280
76.	Hand-scouring	282

FIG.		PAGE
77.	Burdon scouring machine (T. Haley & Co.)	283
78.	Circulum scouring and butt-striking machine	284
79.	Jackson scouring machine	284
80.	Scouring machine	285
81.	Hand-setting	286
82.	Curriers' tools	287
83.	Hot air stuffing drum (T. Haley & Co.)	289
84.	Hot air stuffing drum (Farrar & Young)	290
85.	Hot air stuffing drum (Farrar & Young)	291
86.	Currying shop, Leather Industries Department of the University of Leeds	294
87.	Stoning jack (Turner & Co.)	299
88.	Pendulum whitening machine (Turner & Co.)	305
89.	Areameter (Farrar & Young)	309
90.	The chromatic circle	322
91.	Striking out after dyeing (Messrs. E. & J. Richardson, Newcastle)	325
92.	Polygonal tumbler	329
93.	Single table putting out and striking out machine (Turner & Co.)	333
94.	The "Tabula" setting out and scouring machine	334
95.	Serial table setting machine (Turner & Co.)	335
96.	Morocco finishing shop (Messrs E. & J. Richardson, Newcastle)	336
97.	Embossing machine	337
98.	The "Altera" embossing machine	338
99.	Printing machine	339
100.	Graining machine	340
101.	Level bed glazing machine	341
102.	Glassing machine	342
103.	Fluffing machine (Farrar & Young)	343
104.	Currying seal skins (Messrs. E. & J. Richardson, Newcastle).	347
105.	Slocomb staking machine	359
106.	Bower's chrome glazer (Huxham & Brown's)	361
107.	Preparing seal skins for enamelling Messrs. E. & J. Richardson, Newcastle)	381
108.	Kjeldahl apparatus	398
109.	Extraction of fat from leather by means of Soxhlet apparatus	401

THE MANUFACTURE OF LEATHER

CHAPTER I

HISTORICAL AND INTRODUCTORY OUTLINE

It is always a fascinating occupation to trace the history and to note the origin of a great industry, to study the gradual development in the processes employed in connection with it, and to notice the various outstanding steps in the evolution of more efficient methods. In connection with the leather industry, however, we are met at the outset with the difficulty that the origin of this most interesting occupation is altogether prehistoric, there being little doubt, in fact, that this practice was one of the earliest attempts of man to make use of his available materials. The treatment of animal skins to fit them for useful purposes is a practice which seems to exist wherever mankind has been found. In China the manufacture and use of leather dates back to the remotest eras of its very ancient history, in the more recently discovered continents of America and Australia the curing of skins was found to be well known and widely practised, and even in the most ancient of the Western civilisations the preparation of some kind of leather seems always to have had a place in human skill and knowledge. The Egyptians, who formed the first civilised nation of history, have left considerable evidence, both as relics and drawings, of their very early acquaintance with the dressing of skins, including vegetable tannage, the dyeing, painting, gilding, and embossing of lighter leathers, and the manufacture of shoes, straps, aprons, and other useful articles from the leathers so prepared. The methods of preparing such leathers were also well known to the early

Babylonian and Persian civilisations, and at a later period were also practised by the Greeks.

Under the great Roman World State the manufacture of leather, like many other useful industries, made considerable headway both in the various processes employed and the extent of their use. Pliny mentions that gall-nuts, bark, and sumac were used as tanning materials. The fall of the Roman Empire brought about a decided check on the development of all the arts and industries, including that of leather manufacture, but a good deal of the existing knowledge continued to spread, and gradually reached the Hun, the Russian, and the Teuton. The Moorish invasion of Spain also, in the eighth century, introduced into Europe again the manufacture of the more artistic leathers. From Cordovan or Spanish leather, famous in the eleventh century, our present "morocco" was evolved, and in the fourteenth century leather dyeing and embossing reached considerable perfection in Western Europe.

Although it is certain that the process of vegetable tanning is exceedingly ancient, it is almost as certain that this was not the most primitive method, and that the curing of skins by smoke, by treatment with oils and fats, and by merely sun-drying, are methods even more ancient. Processes such as these, still in use in many of the less civilised parts of the world, leave us in little doubt of the origin of leather manufacture, in spite of the absence of any written historical records. Leather, indeed, is often mentioned as one of the earliest materials for writing upon, though there is considerable doubt whether such leather was in any sense "tanned," and in many cases there is no doubt at all that the material referred to was very closely similar to our present parchment. The manufacture of "tawed" or alumed leather was introduced at a much later date than the vegetable tannages, and was for a considerable period confined to a few localities in which the tawing materials were readily obtainable.

It will be readily seen from the preceding historical outline that the manufacture of leather has been for many ages a purely empirical industry, and that improvements in the methods employed have been in consequence exceedingly few, and slowly introduced into general use. The last century,

however, has witnessed not only vast developments in pure science, but also the commencement of a new era in the history of the human industries, and just as science has applied itself to the manufacture of soaps, dyes, metals, etc., so also has the manufacture of leather become a branch of chemical technology. This transformation from an empirical art to a scientific industry has been, of course, slow and gradual, and confined almost to the last half-century, not being even yet by any means complete. It is fully a hundred years since it was first recognised by Sir Humphrey Davy and others that the process of tannage was a chemical matter, but the real application of chemistry to leather manufacture began much later, the first definitely scientific advances in the industry being mainly of a mechanical character, involving the introduction of machinery and other labour-saving appliances. The application of chemical science to the manufacture of leather has chiefly resulted in the introduction of new materials, in greater efficiency of working and economy of production, in quick process, in the analytical treatment of both raw materials and finished goods, and in the more accurate control of the various processes, rather than in any outstanding improvements in the quality of the goods made by the time-worn methods, and it is also responsible for a new class of leather altogether, viz., chrome leather, which has already taken its place in the front rank of present-day leathers.

The writer has thought it very desirable that some brief outline should also be given in this chapter of the various stages and processes in the manufacture of the leathers which are spoken of in greater detail in the later parts of this volume. It has been stated already that "leather" consists of the animal skin prepared for application to useful purposes by treatment with various processes of empirical origin. All these processes have for their object the conversion of the readily putrescible skin into an insoluble and more lasting material, one which is not only less subject to putrefaction and decay, but which possesses also considerable strength and pliability. It will be readily understood also that the nature of the leather produced is varied very considerably by the

character of the processes by which it is produced, and that these processes are varied deliberately according to the purpose for which the leather is required.

The first process is generally that of "soaking" (Chap. VI.), which involves the cleansing of the skin from blood, dung, dirt, and temporary preservatives by treatment with water, any previous dehydration being now counteracted by a partial swelling.

The next process, except for the dressing of furs and some other skins, is that of "unhairing" (Chap. VII.), by which the hair is removed from the skin by the root. This is brought about by first treating the goods with the hydrates and sulphides of calcium and sodium, milk of lime being most generally used, and causing in this way the destruction of the epidermis of the skin, including the hair root, and the "plumping" of the dermis or true skin, which brings about a separation of the hide fibres. A similar result can be obtained by "sweating," in which process the goods are kept moist and warm in an enclosed chamber, bacterial influence being in this case a more prominent factor. Whichever method has been used, however, both the epidermis and loosened hair are removed by scraping over the "beam" with a blunt two-handled knife. Any animal fat or flesh is removed also at this stage with a sharp knife or machine, and any other necessary trimming brought about.

The "deliming" (Chap. VIII.) which follows varies largely in character according to the class of leather required. Heavy leathers are either treated with suitable dilute acids, or merely washed in water, whereas the finer leathers undergo a little-understood fermentative action, involving a more thorough removal of the lime and a complete relaxation or "pulling down" of the plumped skin, which treatment causes the production of a much softer leather. When an infusion of the dung of fowls is used for this purpose, the process is called "bating," but if dog-dung is used, as for the lightest leathers, the process is termed "puering." Either of these processes may be followed by "drenching," which is an immersion in a bran infusion, the organic acids formed by its fermentation completing the neutralisation of the lime, and even

swelling the skins slightly; the bran itself acting also as a mechanical cleanser.

The "tanning" of the hide or skin follows immediately after the deliming processes, and in the case of the vegetable tannages (Chaps. IX.—XVI.) consists in soaking the goods in infusions of the vegetable tanning materials, of gradually increasing strength in "tannin," which is a name given to all those astringent phenolic colloidal bodies which bring about the desired conversion of "pelt" into "leather." This treatment extends over some months for the heavier leathers, and for several weeks in the case of light and dressing leathers.

The finishing processes (Chaps. XX.—XXIV.) nearly always involve the use of a certain amount of oil or fat, and, with the exception of sole and fancy leathers, the process of "currying" (Chap. XXII.) is undergone, in which the goods are stuffed with fatty matters, thus causing both pliability and impermeability to water. Many of the lighter leathers are dyed (Chap. XXIII.), and then undergo special glazing and finishing processes.

The mineral tannages (Chaps. XVII. and XVIII.) include, first of all, the "tawing" process, which consists in treating the goods with a mixture of alum and salt and subsequent finishing with oily filling materials. The chrome tannages also fall in this division, the tanning of the pelt being accomplished either by drumming with a "basic" chromic salt, as in the one-bath process, or by treatment first with chromic acid and then a reducing agent, as in the two-bath process. Chrome leather made by either of these processes is "neutralised" by the action of some weak alkali, and subsequently dyed and "fat-liquored," this last operation being a treatment with an emulsion of soap and oil.

The aldehyde tannages (Chap. XIX.) include "chamoising," which is a treatment of the pelt with marine oils, the aldehydes formed by their oxidation causing a true tannage of the skin; the manufacture of fat tanned leathers by drumming the pelt with soft fats and greases, a less perfect tannage taking place, but a more complete coating of the hide fibres with oxidised oil products; and also the direct use of aldehydes, as in the manufacture of formaldehyde leathers by Messrs. Pullman's patent process.

CHAPTER II

THE NATURE OF SKIN

Its Physical Structure.—All animals have an external covering for their flesh and fat which goes by the name of skin, and which forms the raw material for the manufacture of leather. The following description is primarily intended to set forth the characteristics of the ordinary ox hide, but the general structure of the skins of all mammals is so very similar that it applies almost equally well to them all. Although the skin is made up of many parts, it is readily divided into two distinct layers, the epidermis and the corium, which are both distinct in their functions and different in their structure.

The Epidermis, epithelium, or cuticle, forms the outer layer of the skin and is much thinner than the corium, over which it lies. The inner portion near the corium is called the *rete Malpighi*, and consists of minute nucleated cells, which increase rapidly by division into two separate nuclei when sufficiently grown. The multiplication of the cells in this way causes the older ones to be pushed nearer the outer surface, and as they approach this they gradually become flat and dry, and are finally transformed into a layer of laminated scales. This forms the outmost *horny layer*, the flattened scales of which are continually worn away and replaced from the rete Malpighi. From the epidermis the hair, horns, hoofs, and similar structures are evolved. The hair, which may be regarded as a type of these formations, sinks for some distance into the corium, but does not properly penetrate it, being completely surrounded by an epidermally constructed sheath, the inner layer of which grows outwards with the hair and forms its cuticle, being scaly in its outmost parts, like the epidermis of the skin. The inner part of the hair consists of spindle-shaped and pigmented fibres, which become soft and round at the hair root, and expand into a bulb. This bulb

has within it the hair *papilla*, which is a projecting portion of the corium containing the blood-vessels by which the hair is nourished. Young hairs are developed from a knob of the epidermis which projects into the corium, or from a thickening

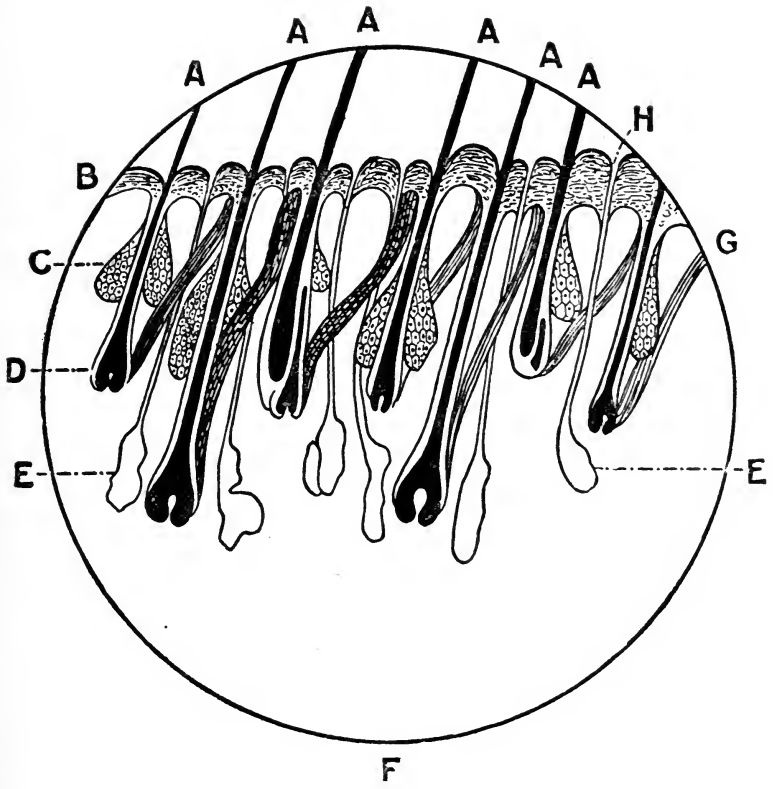


FIG. 1.—Vertical section of calf-skin.

A, hairs; B, epidermis; C, sebaceous gland; D, hair bulb; E, sudoriferous glands; F, corium; G, arrector; H, duct of sudoriferous glands.

at the bottom of the epidermal sheath of an old hair, and being thus more deeply seated, are with difficulty removed in depilation. Every hair possesses an involuntary muscle known as the *arrector* or *erector pili*, which passes from the epidermis to the hair bulb, and contracts under the influence

of fear or cold, causing the hair to assume a more perpendicular position.

The corium, cutis, or derma, which forms the greater part of the skin, has a totally different structure, being chiefly composed of white *connective tissue*, which is fibrous and interlaced, the fibres consisting of extremely minute fibrils cemented together by a gelatinous substance. In between the connective tissue fibres, besides nerves and blood-vessels, there is a

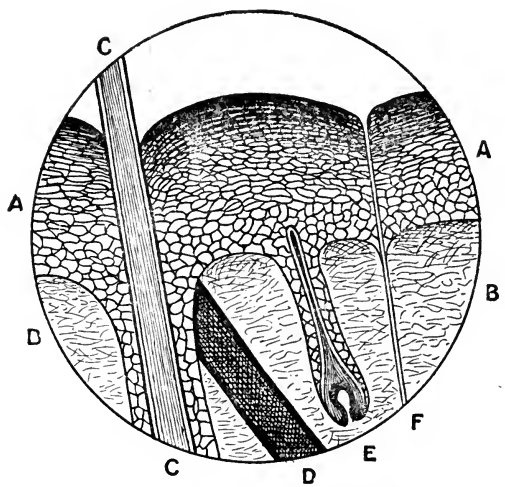


FIG. 2.—Structure of epidermis.
A, epidermis; B, corium; C, hair with epidermal sheath; D, arrector; E, development of new hair; F, duct of sudoriferous gland.

variable amount of *interfibrillar substance*, which gradually changes into fibre, and also a quantity of minute *elastic fibres*, which possess a yellow colour, and are of a muscular character. The connective tissue fibres are the least compact in the central part of the corium, and become much more closely interwoven as the epidermis is approached. This closely interlaced portion is known as the *pars papillaris*, and is that part of the corium which surrounds the hair and its epidermal sheath, and which contains the arrector and the *sebaceous* or *fat glands*. These glands have a cellular or epithelial structure

each cell embracing a nucleus and a considerable proportion of fatty matter, which passes through minute ducts into the hair sheath near the skin surface, and lubricates the hair. In the looser tissue near the hair roots are the *sudoriferous* or *sweat glands*, excretory organs that consist of connective tissue lined with an epidermal layer the cells of which secrete the perspiration. The ducts pass right through the epidermis to the skin surface, the opening being often at the orifice of the hair sheath. Between the corium and the epidermis is the *hyaline* or *glassy layer*, essential for the production of an even-coloured leather and easily damaged by either mechanical or bacterial action. This layer, together with the pars papillaris, constitutes the *grain* of the leather, the characteristic pattern of which forms a ready method for distinguishing the different classes of hides and skins (see Figs. 3—8). That part of the corium nearest the flesh also possesses a more compact structure than the centre, but is connected to the flesh proper by a loose network of *adipose tissue*, which is composed of hide fibres embracing masses of protoplasmic nuclei, each of which has secreted large quantities of fatty matter. These nuclei are also found to a considerable extent in the middle and lower portion of the corium tissue.

FIG. 3.—Cowhide, rough tanned.

For the microscopic examination of the skin structure small and perfectly fresh pieces of hide should be hardened by soaking in several changes of absolute alcohol, and exceedingly thin sections cut by hand with a razor in the plane of the hair roots. The section may be stained by a

twenty-four hours' immersion in a diluted picrocarmine solution, which will give a red colour to the connective tissue and cell nuclei, and a yellow colour to the epidermal cells, gland cells, and elastic fibres. It may be then dehydrated in alcohol, mounted in a xylene solution of Canada balsam, and examined by transmitted light under a low power (1-inch objective). Temporary slides are best made by immersing the sections in concentrated ammonium sulphate solution, which shows up the white connective tissue fibres, or in a mixture of equal volumes of glacial acetic acid, glycerine, and water, which shows up the fat and sweat glands, elastic fibres, and hair bulbs, the connective tissue being rendered transparent. For high-power observations the hide pieces should be first hardened by immersion for a week in a solution of osmic and chromic acids and afterwards dehydrated with alcohol. With this treatment the fatty matter of the glands and adipose tissue appears black. The structure of the grain pattern of leathers may be readily studied under a low power with a good reflected light. Embossed leathers should be wet back and stretched before examination.

FIG. 4.—Cowhide, rolled.

Its Chemical Composition.—Although such a variety of constituents go to form the animal skin, they all belong to one great class of organic bodies, which are known by the general name of *proteids*, all of which are products of animal or plant life and possess an extremely complex chemical constitution. The ultimate analysis of these bodies indicates the same general constitution, and the following figures may be taken

to represent roughly the lowest and highest limits in composition :—

Element.	Per cent.
Carbon	49—55
Hydrogen	6·4—7·3
Nitrogen	15—19
Oxygen	17—26
Sulphur	·3—2·4

The variations noticed in the analyses of any one proteid and the certainty of excessively high molecular weights[1] make it evident that to calculate any empirical formulæ would not only be entirely hypothetical, but altogether useless. The proteids resemble one another in their behaviour with certain reagents, one of which is "Millon's reagent," a solution of mercuric nitrate containing nitrous fumes, a curdy pink precipitate or red colour being obtained on warming the proteid with it. This reaction has been traced to a definite group in the proteid molecule due to tyrosine.[2]

FIG. 5.—Pigskin.

A second characteristic test for proteids is the "biuret[3] reaction," which is a pink colour obtained by adding a trace of cupric sulphate and excess of caustic soda, and which is due either to the biuret radicle or to similar diacidamide groups.[4]

[1] Paal, Ber., 1892, 1202.
[2] p.-oxy. α amidophenylpropionic acid.
[3] $NH(CONH_2)_2$.
[4] Malonamide, oxamide, and glycine amide will give the biuret reaction.

Another general reaction is the precipitation of the so-called "xanthoproteic acid" by boiling with dilute nitric acid (1 : 2) for some days, a yellow flocculent precipitate being obtained which dissolves in ammonia and caustic alkalies with a brown or orange-red colour. The proteids are also extremely similar in their ultimate products of hydrolytic decomposition, breaking up first into simpler molecular complexes known as peptones, and afterwards into still simpler constituents, the chemical constitution of which has been thoroughly investigated in recent years.[1] The peptonisation may be brought about by the prolonged action of hot water, but more quickly by the use of dilute acids or alkalies, by the hydrolytic ferments of the gastric and pancreatic juices, and by the action of the bacterial zymases, as in putrefactive fermentation. The more complete decomposition is accomplished by continued putrefaction and also by the action of concentrated alkalies and acids. The most satisfactory methods for the isolation of these simpler products are due to Kossel and E. Fischer. The former hydrolyses the proteid with hydrochloric or sulphuric acid, which is afterwards removed by cuprous oxide or baryta, and precipitates the cystine,[2] the xanthine bases,[3] and indol derivatives[4] with mercuric sulphate, mercury being removed

FIG. 6.—E. I. goatskin.

[1] Cp. starches, dextrins, and carbohydrates.

[2] An anhydride of thioserine.

[3] Guanine and other purine derivatives.

[4] *E.g.*, tryptophane and skatol acetic acid. These compounds are the cause of the unpleasant odours in the putrefactive fermentation of proteids.

by sulphuretted hydrogen. Phosphotungstic and sulphuric acids are now added to the filtrate, and the "hexone bases," ornithine,[1] lysine,[2] arginine,[3] and histidine,[4] thrown down and filtered off, the acids being removed from the filtrate with baryta. The solution after evaporation below 40° *in vacuo* then undergoes Fischer's process, which consists in treating with absolute alcohol and dry hydrochloric acid gas, thus forming the hydrochlorides of the amido-acid esters. The amido esters are obtained from the hydrochlorides by reducing to a low temperature, treating with very cold caustic soda, and extracting quickly with ether. After the removal of the ether, the esters are fractionally distilled *in vacuo*. Below 100° C. the esters of glycine,[5] alanine,[6] amidovaleric acid,[7] leucine,[8] and pyrollidine carboxyllic acid are obtained, and between 100° C. and 160° C. the esters of aspartic acid,[8] glutamic acid,[9] phenylalanine, serine,[10] tyrosine, and pyrollidine carboxyllic acid.

FIG. 7.—Calfskin.

Certain proteids have also been found to contain carbohydrate groups, and split off sugars when boiled with acids.

[1] 1 : 4 diamidovaleric acid.
[2] 1 : 5 diamidocaproic acid.
[3] 1 amido, 4 guanidinevaleric acid.
[4] Unknown constitution.
[5] Amidoacetic acid, glycocoll.
[6] Amidopropionic acid.
[7] Amidoisocaproic acid.
[8] Amidosuccinic acid.
[9] Amido-glutaric acid.
[10] Hydroxyamidopropionic acid.

Mucine,[1] for example, yields glucosamine. When proteids are subjected to dry distillation a mixture of pyridine C_5H_5N, pyrrol C_4H_5N, and their derivatives is obtained, but it is open to doubt whether these compounds exist to any extent in the original proteid molecule.

There is a very large number of proteids, but, in the absence of any satisfactory criterion of purity for colloid bodies, their accurate analysis and scientific classification is even yet quite impossible. One or two have been obtained in a microcrystalline condition, but there appears to be little hope of progress in this direction, so that it is necessary to fall back on the rather unsatisfactory method of classifying them according to their behaviour with certain reagents, and in this way they may be divided into *albumins*, *keratins*, and *gelatins*. These are differentiated in the first place by the action of cold water, which dissolves the albumins, does not affect the keratins, and only swells the gelatin. When heated in water the gelatin dissolves, the albumins coagulate at rather over 70° C, and the keratins are dissolved only at temperatures above 100° C. On adding acetic acid and potassium ferro-cyanide to aqueous solutions a precipitate is obtained from the albumins and keratins, but not from gelatin. By boiling with alcohol, washing with ether, and heating with hydrochloric acid (specific gravity 1·2), a violet coloration is obtained with albumins, but not with keratins or gelatin.

FIG. 8.—Welsh sheepskin.

[1] From animal secretions.

The albumins, of which the white of egg may be regarded as a type, occur to some extent in the corium of the skin, as the serum in the blood-vessels, and the lymph which permeates the connective tissue and nourishes the whole skin. Their solutions are optically active and lævorotatory, and when quite fresh have a slightly alkaline reaction. The coagulation by heat, which is the most characteristic reaction, occurs usually about 72° C., and is assisted by the presence of some mineral salts. Concentrated mineral acids and alcohol coagulate them in the cold. Coagulated albumins behave in almost every respect like keratins. *Globulins* are albumins insoluble in water, but soluble in weak saline solutions, from which they coagulate at 70—75° C. The myosin of the muscle, fibrinogen of the blood, and vitellin of egg yolk are typical members of this class, but all except the last are insoluble in saturated brine. The *albuminates* are albumins soluble in acids and alkalies and insoluble in water, and are obtained by the action of dilute acids in the cold on the native albumins and globulins. They are precipitated from solution by exact neutralisation of the dissolving acid or alkali, or by the addition of common salt or magnesium sulphate. They are not coagulated by heat, and probably form the first stages of hydrolytic decomposition. The *albumoses*, or albumin peptones, are the next stages in this hydrolysis, being very soluble in water, acids, and alkalies, and not coagulated by heat. They are formed also by the digestive enzymes pepsin and trypsin, and are very similar to the gelatoses and keratin peptones.

The keratins include all horny tissues, and therefore embrace the epidermis proper, and all the epithelial structures of the skin, hair, horns, hoofs, nails, claws, sebaceous and sudoriferous glands and ducts, and also the elastic fibres. They are softened somewhat by water, but not dissolved unless digested for a considerable time at a temperature over 100° C., by which means a slightly turbid non-gelatinous solution is obtained. They are dissolved by the hydrates of the alkali and alkaline earth metals, the rete Malpighi, and other soft keratins with great readiness, and the hair and horns with difficulty and only on heating. The elastic fibres are not

dissolved even by hot caustic potash, but all keratinous matters are dissolved with great ease by solutions of sulphides. They are also hydrolysed by the action of mineral acids, first into peptones and afterwards into amido-acids, etc.

Gelatin[1] is the proteid obtained by boiling the purified hide fibre with water and evaporating the solution. Whether the product is identical with the white connective tissue of the corium is doubtful, but the only certain difference between hide fibre and the best gelatin is that the former is distinctly less soluble in hot water. This perhaps might be accounted for by the peculiar physical condition of the corium tissue, but is more likely to be due to a difference in the degree of hydration, gelatin being a slightly hydrated form of the collagen of the tissue. This latter view is supported by the fact that gelatin dried at 130° C. becomes insoluble even in hot water. The following typical figures show that no striking difference can be demonstrated analytically :—

Material.	Per cent. of				Analyst.
	C.	H.	N.	O.	
Purified sheepskin corium.	50·2	6·5	17·0	26·3	Von Schroeder and Paessler.
Purified oxhide corium.	50·2	6·4	17·8	25·4	Von Schroeder and Paessler.
Ash-free gelatin .	50·0	6·7	18·3	25·0	Schützenberger.

The variations are within those due to the uncertain purity of materials analysed, so that for most purposes we may regard the two substances as identical.

Pure gelatin is a colourless, transparent, and rather brittle solid, devoid of taste and odour, and having a specific gravity of 1·42. It melts about 140° C. with decomposition, and is insoluble in petroleum ether, ethyl ether, alcohol, and benzene. When placed in cold water it swells up very considerably, absorbing about ten times its own weight of water, and

[1] Sometimes called glutin, in which case it must not be confused with the gluten of cereals.

[2] The connective tissue has been chemically termed collagen or ossein.

forming a "jelly," which may be regarded as a solution of water in gelatin. The solution of the gelatin in water, on the other hand, is very slight, but the concentration of both these solutions increases very rapidly with rise of temperature, the surface tension between them diminishing, until the jelly suddenly disappears, and a perfectly homogeneous solution is obtained, which, however, sets again to a jelly on cooling if it contains more than 1 per cent. of gelatin. Aqueous solutions of gelatin are optically active and strongly lævorotatory, but the specific rotation is very variable. Gelatin is precipitated from solution by various reagents, including alcohol, solutions of chromium and aluminium salts and of mercuric chloride, ammonium sulphate when concentrated, slightly acidified brine, metaphosphoric acid, quinone, alkaline or warm formaldehyde, and all vegetable tannins. Alcohol and ammonium sulphate will also dehydrate a water-swollen jelly, but the former will not if the jelly be swollen with acid. The significance of many of these reactions in the processes of leather manufacture will be noticed if it is borne in mind that hide fibre behaves in a precisely similar manner to gelatin, and that when pelt is treated with these reagents it is converted into some kind of leather. The reaction with tannin solutions is typical of the vegetable tannages, and is exceedingly delicate (p. 113), but the precipitate of "leather" is soluble in excess of gelatin solution. When the tannin is in excess the precipitate contains about 66 per cent. of gelatin,[1] but the proportion is variable, no definite compound being known. Rendering gelatin insoluble by means of a chrome alum solution may also be regarded as a type of the mineral tannages, and the action of formaldehyde as representing the aldehyde tannages. The action of acidified salt, ammonium sulphate, and alcohol has its analogy in the pickling process (p. 108), which is a temporary tannage.

Gelatin decomposes hydrolytically in a manner closely similar to other proteids, and yields under the influence of acids, alkalies, or enzymes compounds known as *gelatoses* or gelatin peptones, which are apparently little different from

[1] Böttinger, A., ccxliv., p. 227.

the albumoses or keratin peptones. Many preparations of gelatoses have their origin in attempts to obtain pure hide substance, but almost any treatment of the connective tissue results in a partial hydrolysis. By the action of hot water Hofmeister obtained *hemicollin* and *semiglutin*, which he differentiated by the precipitation of the latter by alcohol and platinic chloride. By the prolonged action of caustic lime solution hide fibre is gradually hydrolysed to a soluble substance which has been named *coriin*,[1] and which is precipitated by careful neutralisation with acetic acid. It is slightly soluble in water and dilute acids, and readily in alkalies and a 10 per cent. salt solution. It is precipitated by tannin, basic lead and iron salts, but not by acidified ferrocyanide, mercuric chloride, copper sulphate, or lead acetate.

By the action of hot dilute acids and alkalies, other soluble gelatoses are obtained, such as the *collin* of Parker and Payne. Generally speaking, the gelatoses are soluble in water, strongly basic, precipitated by tannins, and some of them by alcohol and metaphosphoric acid. They yield on more complete hydrolysis the same products as other proteid matters. Gelatin made from bones, tendons, ligaments, and cartilages possesses the same general properties, and yields the same products of decomposition. *Glue*, which is a mixture of gelatin and its peptones, is used as an adhesive agent. *Isinglass* is the fibrous gelatin from the swimming bladders of the sturgeon and other fish. Russian isinglass is the best, and is nearly colourless, semi-transparent, odourless, tasteless, and gives a very strong jelly. It is noteworthy that jellies can be made also from agar-agar, algin, and similar extracts of various lichens and seaweeds. Such bodies contain little or no nitrogen, and are not proteids.

[1] Reimer, *Ding. Polyt. Journ.* ccv., p. 153.

CHAPTER III

FERMENTATION

The importance of fermentation in the manufacture of leather will be readily understood when we not only remember that many of the materials used are highly organised matter, and therefore easily decomposable or fermentable, but also recognise that nearly all the processes of the industry are dependent upon the action of various ferments for their satisfactory consummation. It will be seen, therefore, that it is extremely desirable some attempt should be made to understand something of the nature of the agencies at work, the conditions under which they operate for weal or woe, and the methods by which we are able to control and limit their action.

The simplest form of organic life consists of the living proteid called *protoplasm*, which is a jelly-like mass capable both of independent existence and of motion, and is well illustrated by the lymph of the human system and the amœba of ponds. This protoplasm, like all living things, requires nutriment to produce its heat and energy, and this it obtains from its immediate surroundings. It uses this food also to build up its system and usually to enclose itself in a wall of cellulose or keratinous matter, thus forming a *cell*. Every living cell has in its protoplasm a nucleus, which for purposes of reproduction is capable of division into two portions, each of which, associated with some of the surrounding protoplasm, goes to form a new cell, as already illustrated in the rete Malpighi of the skin. In multiplying thus the new cells may separate and become quite independent, or they may remain together in chains or masses. Differences also occur in shape, in the cell-wall substance, in the secretions and excretions, and masses of such various cells go to build up the higher forms of animal and plant life, in which every variety of cell has its

own specific functions in the maintenance of the whole structure.

It has been pointed out that the cells which compose the animal system require food, but the substances which are ordinarily supplied are not usually in the form in which they can be readily absorbed, so that chemical changes are necessary to bring them into the desired condition, and these changes, which generally involve the liquefaction, solution, or emulsification of the nutriment and the breaking down of its components into molecules of simpler chemical structure, are brought about by *enzymes*, which are lifeless proteids of an albuminous nature, and which form the class of *unorganised ferments*.

These enzymes, or zymases as they are often named, being devoid of life, possess no powers of reproduction. They are soluble in water, and are coagulated by heat (cp. albumin), being thereby rendered quite inoperative. Their activity is also destroyed by certain antiseptics (see below). Many of them may be precipitated from their aqueous solutions by means of alcohol, and after filtering off may be redissolved in water and again caused to act as active ferments. They are well illustrated by the *ptyalin* of the saliva, which converts starch into sugar, the *pepsin* of the stomach glands, and the *trypsin* of the pancreas, which dissolves fibrin. The mechanism of the chemical changes which these ferments accomplish is still very obscure, but it is known that very small quantities of them are capable of decomposing very large quantities of the bodies on which they operate, and that they are themselves unchanged at the end, so that some analogy is found in the so-called "catalytic actions" of chemistry. Much interesting work has been done in recent years on the *selective action* of these ferments, such as *maltase*, *emulsin*, *invertase*, and *lactase*, on the glucosides and carbohydrates, and it has been suggested that the enzymes are asymmetrical bodies which "fit in" with certain other asymmetrical[1] substances, which are those they ferment, as a key fits in a lock, and where the key will not fit (*e.g.*,

[1] In the stereochemical sense.

invertase or maltase with milk sugar) no action can take place. It has also been shown that with comparatively small quantities of enzyme the decomposition is a linear function of the time, but that with sufficient enzyme it is a logarithmic function and follows the ordinary mass law. That enzymes are not always analytic and hydrolytic agents has been demonstrated by their synthetic production of amygdalin,[1] disaccharoses,[2] and esters.[3]

In plant life these unorganised ferments fulfil the same functions as in animal life (*e.g.*, *diastase* and starch), but when green plants send forth their leaves they obtain most of their nourishment from the atmospheric carbon dioxide by means

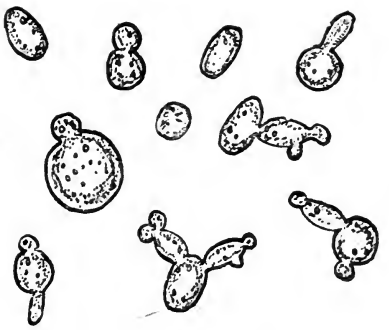


FIG. 9.—Yeast cells.

of their chlorophyll and the sunlight. Certain plants, however, known as *fungi*,[4] have no chlorophyll, and are therefore compelled to obtain their organic nourishment from their immediate surroundings, which they accomplish directly, or by means of the enzymes they secrete. The lower forms of these fungi (yeasts, moulds, and bacteria) constitute the *organised ferments*.

Yeasts (*saccharomycetes*) are simple cells of nucleated protoplasm with a cellulose wall. They multiply by the formation

[1] By *maltase* from glucose and the glucoside of mandelic nitrile.
[2] *Isolactose* by *lactase* on glucose and galactose, and *isomaltose* by *maltase* on invert sugar.
[3] By *lippase*.
[4] Mushrooms, etc.

of "buds" on the side of the parent cells, which enlarge till they become full-grown cells and have themselves buds. This method of reproduction results in groups or chains of cells, but each one provides its own nutriment. The action of yeasts is well illustrated by the ordinary alcoholic fermentation of glucose.

Moulds (*ascomycetes* and *phycomycetes*) are a rather higher form of plant life in which the cells are elongated and remain connected, thus forming stems and branches (*hyphæ*), upon which appear masses of spore-bearing cells. They are often

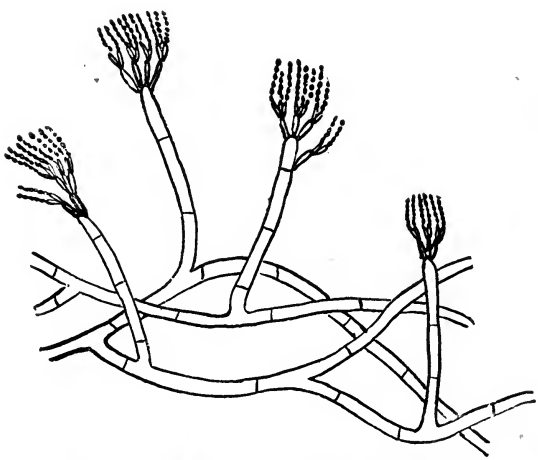


Fig. 10.—Mould (*Penicillium glaucum*).

characteristically coloured, and the cells of which they are composed are not always independent of other cells for their nutrition. Some of these plants are capable of reproduction by sexual fructification. The action of moulds is illustrated often on decaying fruit.

Bacteria (*schizomycetes*) are the lowest forms of the fission fungi. They are simple cells which multiply by lengthening and dividing, but certain forms are capable of producing *spores*, which appear at one end and grow into a new cell. There is an immense variety of species of these fungi, and our knowledge of them is as yet very incomplete. Classification,

therefore, is difficult, but they are often divided into (1) *micrococci*, small spheres, connected or independent; (2) *bacilli*, rods, dumb-bell-shaped, or ovals, often motile; (3) *spirilla*, spirals, usually motile. They are all exceedingly small, requiring a $\frac{1}{12}$ inch objective and oil immersion lens for proper examination. Even then this is difficult, for confusion may easily arise between a dumb-bell-shaped bacillus and a dividing micrococcus, and the spores of the spirilla and bacilli may be taken for cocci. They are recognised by their size, which varies usually between 0·5 and 5·0 μ[1]; by their

FIG. 11.—Bacteria.
A, micrococci; B, bacilli; C, spirilla.

flagellæ, which are filaments used by the motile forms for motion; by their colour, and also their appearance on staining with various basic aniline dyes; by their method of reproduction and the range of temperature within which they can live. Bacteria may be "aerobic," in which case they thrive in the presence of oxygen (or air), which is absorbed by them in oxidising their food; or they may be "anaerobic," in which case they can live only in the absence of oxygen and derive what they need of it directly from their nutriment. The former tend to produce as waste products water, carbonic acid, nitrogen, nitrates, sulphates, etc., which are harmless and without odour, but the latter, being reducing agents, yield such compounds as the hydrides of carbon, nitrogen, sulphur

[1] μ is a micromillimetre (= 0·001 mm.). Some bacteria, however, are ultra-microscopic.

and phosphorus and their organic derivatives, many of which are excessively poisonous to human beings. This is the case with many of the disease bacteria, and perhaps is the reason why bacteriology is better developed on its pathological side. Many bacteria are poisoned by the products of their own work and, unless these are removed, die out, their places being rapidly taken in putrefactive fermentations by organisms more suited to those surroundings. Some bacteria can thrive under both aerobic and anaerobic conditions, and produce different effects accordingly. The chemical effects and physiological actions of bacteria are extremely useful in identification.

It is now well recognised that many of these organised ferments secrete enzymes, and hence that many of the effects noticed are only due indirectly to the fungi. Yeast, for example, cannot attack cane sugar until it is converted into monosaccharoses by the enzyme *invertase*, and it has been shown that the effects of puers are due to enzymes rather than the bacteria with which they are associated. It is in many cases exceedingly difficult to distinguish the two classes of fermentation, for both organised and unorganised ferments are destroyed by heat. They may, however, be differentiated by means of chloroform, which does not at all affect enzyme action, but which will paralyse or kill bacteria. The two classes of ferments may also be separated to a certain extent by filtration through very compact earthenware, such as the Chamberland "candle," which will not allow the passage of many bacteria.

The complex fermentation of nitrogenous organic matter, usually accompanied by unpleasant odours, is generally termed *putrefaction*, and is brought about by bacteria, directly and indirectly, by moulds, and to some extent by the lower forms of animal life (*monads, infusoria*, etc.). No specific fermentation takes place, of course, under such circumstances, but an extremely complex action occurs, the course of which is never exactly repeated.

The first stage of this involves the action of aerobic bacteria (*B. liquefaciens magna*, etc.), solid matter being liquefied and but little odour produced. The second stage permits the action of the true putrefactive, and facultatively anaerobic

bacteria, of which *Proteus vulgaris* and *P. mirabilis* are the commonest. These do not secrete any enzyme, but ferment by direct action. *Bacillus prutrificus*, which attacks fibrin, is also active. Other bacteria follow, *Proteus zenkeri*, etc., which only attack peptones, and the final stages of decomposition are extensively effected by flagellate monads. From recent investigations of such fermentation processes it has become "very probable that specific organisms ferment the different albuminous compounds in the same way that different carbohydrates are each decomposed by specific ferments." [1]

All ferments are affected, in greatly varying degrees, by certain bodies called *antiseptics* or *disinfectants* such as mercuric chloride, salicylic, sulphurous, and boric acids, phenols, cresols, naphthols, and chloroform. These destroy the ferments or paralyse their activity, thus rendering their surroundings sterile. They are used extensively both to arrest and to prevent fermentation, or to allow only the class of fermentation which is desired. As moisture is essential and a high temperature fatal to fermentation, the processes of drying and heating are both extremely useful in preventing it.

In the manufacture of leather various fermentations are encouraged and discouraged. Hides and skins are kept from putrefaction by drying and by the use of salt and other antiseptics (p. 28). In soaking an attempt is made to cleanse and soften the hide without fermentation unless it is extremely hard, in which case the bacterial solvent effect of a putrid soak is sometimes considered an advantage (p. 50). In depilation the hide is placed in a lime liquor, which, in addition to its chemical action, acts as an antiseptic to many of the putrefactive bacteria, but allows the fermentative action of those which attack the epidermis and hair root. This is also accomplished, less perfectly, in an ammonial atmosphere by the "sweating" process (p. 57). In bating and puering, the hide or skin is immersed in a nutrient medium which especially favours the growth of certain bacteria whose enzymes and products of decomposition produce the required effect. The temperature is also adjusted to assist in the same direction

[1] Wood, J.S.C.I., 1906, 109

(p. 97). The action of the drench is due to the weak acids and gases produced by the successive action of certain enzymes and bacteria (p. 99). In the tan-house bacteria are useful in acting on the sugars to produce the acids which neutralise the lime and swell the hides, whilst yeast and moulds are injurious, acting destructively both on the acids and on the vegetable tanning matters. Moulds and bacteria are also the cause of leather being destroyed in the sheds by "heating," and the former are also apt to commence their action upon leather which is being dried too slowly. Many defects in finished leathers (spots, weak grain, etc.) are due to the injurious effects of bacteria which have been accidentally introduced into some of the processes employed (p. 50).

CHAPTER IV

HIDES AND SKINS

The commercial distinction between hides and skins is based upon the size and age of the animals, and the class of leather for which they are intended to be used. Hides, the name given to the external coating of the larger and adult animals, are used for the manufacture of sole and heavy leathers, and are obtained from the ox, heifer, bull, cow, buffalo, horse, hippopotamus, walrus, and include also "kips" (p. 36), but as the ox is the most commonly used, the word "hide" is often used as if the term were restricted to that animal. Skins are obtained from the smaller animals, such as the sheep, goat, seal, pig, deer, and the calf, and also from alligators, serpents, lizards, fish, etc. These are used for the manufacture of the lighter and fancy leathers.

Hides of the ox, to which the following remarks chiefly apply, are procured largely from the slaughter houses of Great Britain, being sold by auction in the principal market towns, and in these cases no attempts are made to "cure" or preserve them from putrefaction; but there are now immense quantities of hides which come from all parts of the world, and it will be clear from what was said in the previous chapter, that if they are to arrive in this country in a satisfactory condition for tanning, some precautions are absolutely necessary to keep them preserved from decomposition and decay. There are several **processes of curing** in operation, and an outline of the chief of these is now given.

One of these consists in merely *drying* the hide, which in this way becomes hard and horny,[1] the absence of moisture preventing the development of any putrefactive bacterial action. In places where preservatives such as salt are

[1] This fact has given rise to the term "flint hides," which is sometimes applied to this class of goods.

dear, and where the distance for land transit is considerable and weight therefore of importance, this method is often the only one really practicable, but it is a process which is difficult to carry out satisfactorily. It is essential that the drying should be even and gradual, but rapid, and the best drying is done therefore by means of a good draught in the shade. If the drying is too slow putrefaction will begin; if it is too rapid the hide will be merely caked on the exterior whilst the interior is still moist and putrescible, and there is a strong probability also that in some parts the fibrous structure will be quite destroyed. With this method of curing there is always much more difficulty in soaking and softening the hides than there is with any other class of goods, and where the drying has been faultily carried out, the difficulties are much greater in the soaking, and the damaged parts are often irreparably ruined in the unhairing. The opportunity for bacterial attack can be reduced to a minimum by the use of antiseptics, such as carbolic acid.

Salting is one of the most satisfactory methods of curing now in use. Common salt possesses considerable hygroscopic qualities and can withdraw from the hide with great readiness a large proportion of its moisture, and being also a mild antiseptic, hides well preserved in this way will keep almost indefinitely. The method is employed extensively for the preservation of "packer hides" in the stockyards of the United States. The hides are trimmed, and stored in cool cellars in packs of which the sides are kept higher than the middle by folding, so that the brine that is formed can only escape by passing through the goods. Each hide requires about 25 per cent. its weight of salt, which should be spread evenly, and chiefly on the flesh side. The cure should take about a fortnight, and when complete much of the salt is recovered and mixed with fresh salt for the cure of a fresh pack. If instead of white crystallised salt an impure rock-salt is used, the iron which is often present is very liable to cause "salt-stains" on the hides, and similar stains are produced by bacteria when the cure has not been efficient. *Brined* hides are cured by steeping in a strong solution of salt, and are much less perfectly preserved.

Dry salting is also a very efficient method of curing and is now used to a considerable extent. It is a combination of the drying and salting processes. The hides after flaying are hung up in a cool room and partly dried. They are then spread out on the floor and piled flesh side up with salt between, the edges being folded slightly inwards. When the brine has formed it is run off, the hides suspended again and, dried till in a rubbery condition and then resalted. The hides of the small Indian cattle come to this country in a dry salted condition ("kips"), but the cure is accomplished by an earthy sodium sulphate instead of sodium chloride (see p. 36).

Criteria for selection. The nature of the hide is much influenced by the breed of the animal, its food, and the conditions of its life. Those animals which are exposed to all winds and temperatures, especially those from hilly regions, and districts where there is opportunity to roam about, yield much the best hides for the leather manufacturer, being thick, compact, smooth in grain, and of good texture; whereas those which are bred for their milk-producing qualities, such as the Dutch animals, and others from lowland regions, give poor thin hides. Stall fed animals are objectionable from the tanner's standpoint, being often very badly ribbed in the neck, and diseased animals also give hides of very poor quality.

The age of the animal has also a very great influence on the resulting hide. *Calf skin* is obtained by killing the animal at the age of about six months; it is very soft and milky, and possesses a characteristic fine grain and compact texture. It is used extensively for the manufacture of leather for boot uppers.

The hide of the *ox* and *heifer* are intermediate in texture and substance and give much the best results for sole leather, being well supplied with interfibrillar substance. *Bull* and *cow* hides, on the other hand, are very rough and wrinkled, showing extremely coarse fibres and a lack of interfibrillar substance, producing therefore a thin non-waterproof leather. They are used for boot uppers, portmanteaux, etc. Bull hides are apt to be thin in the back and thick in the neck and belly.

The quality of the hide is also much influenced by the care taken in flaying. This operation should take place immediately

the animal is killed, and should aim at detaching as much of the flesh and fat as possible without gashing the hide itself. The process requires a certain amount of dexterity, and should be accomplished, if possible, by experienced persons. The possibility of blood stains, especially in hides to be cured, should be carefully guarded against. Where the hides are not to be cured they should be sold as soon as possible, or lightly salted, for delay involves putrefaction, and hides which are "slippy," *i.e.*, those in which the hair can be easily pulled out by hand, are of much less value to the leather manufacturer.

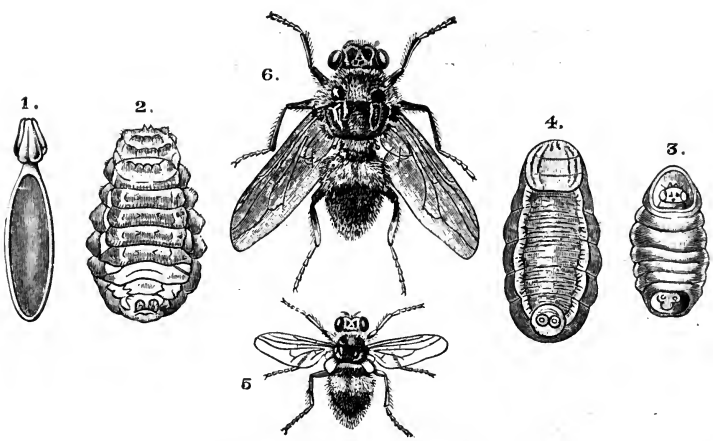


FIG. 12.—Warble Fly (*Hypoderma bovis*).
1, egg; 2, maggot; 4, chrysalis case; 6, fly, magnified (Brauer); 3, 5, chrysalis and fly, natural size (B. Clark).

Defects and injuries, however, unfortunately occur before the animal is killed, and have considerable bearing on the value of the hide. Scratches due to hedges and barbed wire, drovers' goad marks, scabs, tar marks, and brands, all (especially the last) reduce considerably the worth of the hide to the tanner. Another serious defect in hides is the occurence of *warble holes* or *marks*. These are caused by the Ox Warble Fly, or Bot Fly (*Hypoderma bovis*) which is a two-winged fly, about half an inch in length, banded with thick hairs of different colour, somewhat like the humble bee. The female of the English species lays its eggs on the backs of the animals in the hair,

and the larva when hatched eats its way into the skin, making in this way a sore or swelling, and feeds on the matter caused by this irritation. As the maggot develops the sore "ripens," and opens in the middle, showing the breathing spiracles of the nearly mature larva, which when fully grown comes out at this "warble hole," falls to the ground and creeps to some stone or shelter to pupate. It stays in the chrysalis state from twenty-six to thirty days, and then comes out as the imago or perfect insect, which continues the infestation. This pest sometimes gives rise to several hundred "warbles" on one beast, causing much pain and occasionally death. The warbled hides also sell at a decidedly lower price than the undamaged, and leather made from the former is obviously useless where it is necessary that the material should be water or wind tight.

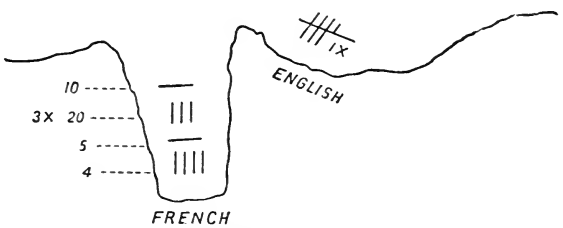


FIG. 13.—Tail-weights (79 lbs.).

It is therefore of some considerable importance to take some preventive action against the insect in the interests of the farmer and leather manufacturer alike, and this may be done by squeezing out the maggot by hand, or killing it by a small application of mercurial ointment, and also by applying a mixture of sulphur, tar oil, and train oil along the spine of the animal, the smell of this mixture driving off the flies and thus preventing the eggs being deposited. It has been demonstrated that if thorough measures are taken in this way, any district may in the course of a few seasons be completely cleared from the pest.

As hides are bought and sold by weight, they are classed in the principal markets in this manner, the weight being marked on the tail end as shown in Fig. 13. The weight of obtainable leather being approximately proportional to the

weight of "pelt," which is the hide unhaired and swollen with lime, hides should be chosen that give a good yield of pelt, and it is clear that those with short hair, and those which have small horns, or which are weighed without horns, are best in this respect, and it is often economical to buy these at a nominally higher price. With ordinary market hides there may be a 90 per cent. yield of pelt, varying, however, with the time of year, but it is necessary to remember in buying that salted hides may yield 120 per cent. of pelt on account of the

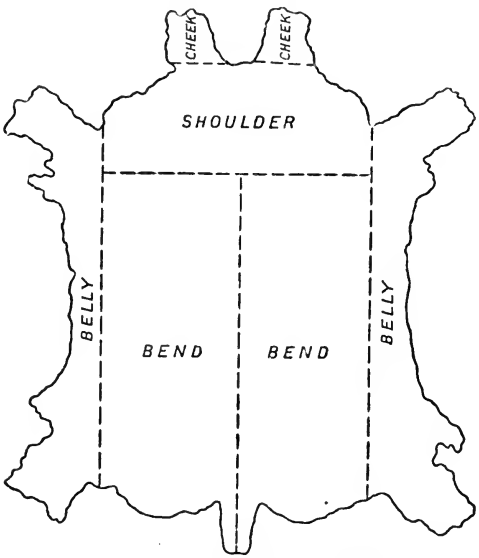


Fig. 14.—Rounding a Hide.

dehydration involved in the curing process. It is desirable, moreover, to keep an eye on the amount of salt which is being bought with the hide, for this may vary between 20 and 40 per cent. Brined hides do not come up to salted hides in yield of pelt.

It is usual also to "round" the hides after soaking and unhairing, thus cutting them into "butts," "shoulders," and "bellies"; the butt, when cut down the middle of the back, gives two "bends," as shown in figure, and as the butt is much the most valuable portion it will be readily understood that

selection should be made to give the best percentage yield of this part. From this standpoint, animals which have short necks and legs, and which do not run thin in the flank are the best, and should give butts fully 50 per cent. of the pelt weight, especially in the autumn.

The chief sources of supply are the home markets, South America, and the Continent.

Amongst the *English* breeds the "Herefords" yield some of the best hides. The animals have white faces, bellies, and tail tips, and carry medium-sized horns which are nearly horizontal. Their hides are obtained in the Midland markets, and unless fed for show purposes are very free from grease and of good texture. They yield usually quite 50 per cent. of butt pelt, and give stout level-grained shoulders. They are very suitable for sole and harness leather. "Shorthorns" is a general name which covers many varieties of similar breeds in England, Scotland, and Ireland, and there is consequently great variety also in the quality and texture of the hides obtained from them. The animals are of a red, white, or roan colour, with small neat horns, but on account of their high feeding for show purposes, some are apt to be very greasy. The "Devons" (N. Devons, S. Hams, etc.) are beautiful cattle of medium size and dark red colour, excepting the white udder, tail tip, and nose. The hides are well grown and of good texture, but often very badly warbled, which spoils them for chrome and high class dressing leather. The "Sussex" cattle are really a cross of Devons with other cattle. They are larger, stronger, more darkly coloured, but less proportionate than the Devons. Their long necks and legs lower the percentage yield of butt. The "Suffolk Red Polls" are a hornless red cattle found throughout East Anglia. The hides give a clean well-grown butt, and the cowhides are suitable for dressing leather and chrome work. The "Channel Islands cattle" (Alderneys, Guernseys, Jerseys) are well groomed and somewhat delicate cattle with short hair, small heads and legs. The hides are yellow and very thin, but usually possess a good undamaged grain with no warbles; they are therefore very suitable for some classes of chrome and dressing leather. The "Longhorns" ("Cravens") are the largest British breed, but are dying

out. They have large down-curving horns, and in colour are dun deep red, roan, or pied. These hides yield good stout butts. The "White wild cattle," which are the ancient breed of Britain, are now nearly extinct; only a few degenerate herds now remain. Of the *Welsh* breeds the North Wales Black (Carnarvons, Cardigans, etc.), the South Wales Black (Pembrokes, etc.), the Castle Martin White, and the Glamorgans are the principal varieties. They will all yield good stout butts.

The *Scotch* breeds are also important. The "West Highlanders" ("Kyloes") are the hardiest race in Britain, possessing long, thick, shaggy and glossy hair and a hairy head. They are chiefly black but are also dun, brown, and brindled. They have big, upright and wide spreading horns with black or red tips, and are great in body and short in leg. The "Polled Aberdeen-Angus" are a black hornless cattle with smooth coats. The "Galloways," another polled Scotch breed, are much like the Aberdeen-Angus, but have woolly coats of rough and rather curly hair. They have a white head, short neck, straight back, and short legs. All these three breeds yield good, well-grown hides. The "Scotch shorthorns" are a cross with the Aberdeen-Angus, but are in colour red, pied, dirty white or brindled. Their hides are amongst the best procurable for sole leather purposes, being well grown, thick, short in neck and leg, small in head, and usually well flayed. They yield over 50 per cent. of butt and up to 24 per cent. of shoulder. The "Ayrshires," which are the best milkers in Scotland, are red, white, black, mixed, or patchy; their hides are not so good, being big in belly. The "Orkneys" and "Shetlands" are small hardy cattle with shaggy coats. Their hides are not of great commercial importance.

The "Kerrys" are the only distinct breed of *Ireland*. They are small and hardy, usually black but sometimes brown or red and with white streaks on the belly and udder. They have short hair and thin wide-spreading horns. They give good light butts for sole and dressing leather. The "Dexter-Kerry" is somewhat smaller and stouter. Other hides (from Shorthorns, etc.) come from Ireland, but are mostly thin, light, coarse textured, and badly flayed. These are suitable only for cheap light sole bends.

The *South American hides*, which are salted or dry salted, are excellent in breed, carefully slaughtered, well flayed, thoroughly cleansed, and well cured, but they are objectionable on account of their brand, which is not only large and deep but is also on the most valuable portion of the hide. These brands, which it seems impossible to avoid, are however usually on one side only, so that one clear uninjured side can always be obtained. Those from Buenos Ayres are considered the best, whilst those from Uruguay are also good. Hides from the Rio Grande are often inferior and tick pitted. There are three classes of these hides: "Saladeros," which come from the large slaughtering establishments, and are well flayed and cured; "Estancias," which are killed at ranches up in the country, and are not so good; and "Mataderos," which are killed by town butchers and are often ill flayed and imperfectly cured.

The *Central American supply* consists mostly of flints from Brazil, Texas, Mexico and other Central American States. They are difficult to soften satisfactorily, and are mostly used in the United States for sole leather (acid hemlock tannage).

The *Chicago packer hides*, wet salted and well flayed, are not very thick, and are mostly used in the United States for dressing leathers. "Natives" are hides from native steers, and usually free from brands; they are chiefly used for harness and belting leathers, but if "spready" are used for the tops of carriages, and if from "butt-branded steers" they are used for sole leather (union tannage). "Texans" are hides from steers from Texas, and make the best sole leather of the packer hides; they are nearly always badly branded. "Colorados" are branded also; they are used for upper leather.

The *Continental hides* are usually salted and without horns and tail bones. Bavarian highland hides are celebrated for their thickness and evenness of growth. They are well grown, tightly built up, and possess a fine smooth grain. Usually, also, they are well flayed, and hence are especially liked for army work and for heavy belting. Hides from the Swiss Alps are similar to the Bavarians, but have shoulders not quite so thick. Italian hides are from a smaller breed of animal; they are shorter in the butt, but thicker. They also

are hides of even growth, compact texture, fine grain, and are well flayed. Spanish and Portuguese hides are also good, but somewhat liable to scratches and spots. Scandinavian hides rank high, being well grown, well flayed, and of even texture. Hungarian hides are often very large, but are tight in texture, well flayed, and give good grain. Hides from lowland regions (Berlin, Cologne, Holland, etc.) are long in shank and not particularly well grown. They are mostly used as dressing hides. French hides are often badly flayed.

"*E. I. kips*," which are almost a class to themselves, are obtained from a small breed of Indian cattle killed when one or two years old, and are largely imported into this country in a dry salted state. The cure is with a sodium sulphate earth,[1] which is mixed into a paste with water and painted on the flesh with a brush, the hide being then dried in the sun. This is repeated several times before export. They are tanned for boot uppers, " waxed kip butts," satin kip, box calf imitations, etc. A large number are now imported in the rough-tanned state.

Buffalo hides, obtained from the true buffalo (*Bubalus buffalus*), which is common throughout Asia and Eastern Europe are imported into this country for the manufacture of pickers, belt leather, and sole leather.

Horse hides, obtained chiefly from South America, are tanned for boot uppers and enamelled leathers, the butts being made into " crup " leather. They are also " tawed " for whip thongs, aprons, etc.

Hippopotamus and Walrus hides are imported to a small extent, and after a long tannage become exceedingly thick and porous. The leathers are principally used for polishing and burnishing implements, and for brakes.

Skins are obtained from many animals, but most extensively from the common *sheep*. Much of what was said as to influence of food, health, breed, and surroundings on the quality of hides, applies also to these skins. Sheep exposed to adverse climatic conditions yield the best pelts, whilst those which are carefully bred for their wool give poor thin skins. Devons and Cheviot crosses, for example, yield poor wool, but

[1] Procter and Towse, J.S.C.I., 1895, 1025.

give good pelts, whereas the Leicesters, Lincolns, and South Downs give excellent wool but often only poor skins. It has been noticed also that better pelts are obtained some little time after the animals have been shorn.

The leather manufacturer usually obtains his sheep skins from the *fellmonger*, whose business it is to remove the wool, which is the most valuable portion of the skin.

The fellmonger divides British sheep into Long Wools, Short Wools, and Mountain Breeds. Of the *Long Wools*, the "Leicesters" are an important class, and are found extensively distributed throughout the north of England (Border Leicesters, Yorkshire Leicesters, etc.), and to some extent in the Midlands and in Ireland. They are great favourites with stockmasters for crossing. The "Lincolns" are found only in the Lincolnshire wolds. They have white faces and shanks and yield a big pelt of good grain. They are noted for their great weight of fleece. The "Cotswolds," which are the largest British breed, are found only in the Cotswold Hills, and have white faces and legs and no horns. They yield a very long and fine wool, but the pelts are often very greasy especially in the back. The "Devons," found in the valleys of Devon, Somerset, and Cornwall, yield strong wool of fair length and somewhat peculiar colour. The pelts are good and quite white, but are not so big as those previously mentioned. "Kents" (Romney Marsh) are somewhat larger than Leicesters, with white faces and legs and no horns. They have also a tuft of wool on their heads. Good pelts are obtained from them. "Roscommons" are the principal Irish breed, but are much crossed with the Leicesters. They yield long silky wool and wide pelts, which are somewhat "leggy."

Of the *Short Wools*, the "South Downs" are amongst the most important. They are small and well shaped, having grey faces, fine wool, and no horns. This variety yields fair pelts and the best mutton, but is a rather delicate sheep, and therefore has been much crossed with Cotswolds and other breeds. "Suffolk Downs" are cross-bred Downs, found chiefly in the eastern counties, with black faces, heads, and legs. They yield fair pelts. "Oxford Downs" are similar crosses but larger. "Hampshire Downs" are cross-bred

downs, also similar to the above, but with heavy black faces. "Shropshire Downs" are cross-breds which are rather hardy, and are heavier in wool. "Somerset and Dorset Horns" are a very hardy and prolific short-woolled breed. They have white faces, nice horns, and wool and pelts of intermediate quality. "Ryelands" have short white wool and no horns. "Clun Forest" ("Radnors") have speckled tan faces, coarse wool, and yield fair pelts.

Of the *Mountain Breeds*, the "Cheviots" yield very good pelts. They are a middle-woolled breed, which grow much hair amongst the wool, and possess white faces and legs and no horns. They are long in body and very hardy. "Black Faces," found in the mountainous parts of North England, Lancashire and the Scottish Highlands, grow long, open and coarse wool, but give good pelts. "Herdwicks," found in Cumberland and Westmoreland only, are rather similar "Limestones" are a good-sized white sheep with large horns, fine wool, and good pelts. "Lonks," which are the largest mountain breed, give a big pelt, good mutton, and coarse wool. They have horns and black faces. "Exmoors" and "Dartmoors" are small breeds, which yield tough pelts and strong wool. The "Soft-Woolled Mountain sheep" produce white, fine soft wool, and a very small pelt. "Shetlands" are rather wild animals, with brown-grey fleeces, much hair, and good pelts. The "Welsh Mountain sheep" yield poor wool, but a small fine-grained pelt.

Sheep skins are usually classified by the leather manufacturer according to their size. *Small skins* are obtained from the Welsh mountain sheep, from those of the mountainous districts of England, and also from young sheep and certain foreign sheep. These are mostly tawed and used for shoe linings, gloves, etc. The Welsh mountain sheep are liked for roller leather manufacture. *Medium skins* are from the North and South Downs and Scottish sheep, and are tanned to make "roans" (p. 208), a kind of imitation morocco leather. *Large skins*, from the Leicesters, Lincolns, Cotswolds, etc., are extensively used for the manufacture of "skivers," which are made by splitting the limed skins in two (p. 279) and tanning the grain with vegetable tanning materials, the flesh splits

being made into chamois leather by treating with oil (p. 247). Skivers are made into hat linings, pocket-books, camera bellows, etc. A large number of these skins are also made into "basils" in the west of England by tanning with oak bark and extracts, and in Scotland and the north with larch bark. Basils are used for slipper leathers, etc. Some of these skins are also tawed for aprons and for druggists' "white leather," and others dressed with the fur still on and used for mats, rugs, and similar articles.

There are a considerable number of imported sheep skins, chiefly from South America, Mexico, the Cape, Australia, and New Zealand, but the two last-named are beginning to tan their own skins, and we now import them to some extent in the tanned state. Tanned sheep skins are also imported largely from the East.

Lamb skins are very largely tawed for the manufacture of "glove kid," the skins being obtained both at home and from Italy and the south of France. These skins yield pelts with an exceedingly fine grain and delicate texture, and will dye very uniformly, but it is essential that the lambs should be slaughtered when about a month old, for these special characters gradually disappear as the animal gets older. Lambs killed whilst having still their characteristic short curly wool have their skins dressed for "Astrakan."

Goat skins yield a leather which possesses a far greater durability and a much superior texture than that obtained from the sheep, and they are therefore in great demand, supplies coming from all parts of the world, usually in a dried or salted condition. Those obtained from the Cape goat are often larger, thicker, and stronger than the others, but, being imported in the dry state, they are not always in a perfectly sound condition. The skins of the Swiss goat are fairly large, clean fleshed, well grown, have a fine grain, and are made into a strong durable leather. The Abyssinian skins are exceedingly tough and compact, and yield a bold-grained leather. The Balkan and Bavarian skins are rather smaller, but are plump and give a fine close grain. Mexican skins have also a high character, but Scandinavian goats yield skins which are very poor and flat. Goat skins also

come from the East in a tanned state (E. I. goat). An immense quantity of these skins are manufactured into various kinds of morocco leathers, which have a very characteristic grain and are capable of taking up evenly some very brilliant colours. They are used for a great variety of purposes, bookbinding, upholstery, and many fancy articles. Indian dried goat skins are largely imported. They are rather small, and are used extensively for the manufacture of light chrome leathers.

Kid skins are imported from Italy for the manufacture of glove leathers by tawing. The kid skins of France and Ireland are also held in high esteem. As with lamb skins, it is exceedingly important that the skin should be obtained before the animal begins to feed extensively on vegetable matter, for when this commences the extreme fineness of grain and delicacy of texture are rapidly impaired. Tawed kid is also used to some extent for the manufacture of light shoes and slippers.

Seal skins are obtained from the true seal (*Phoce Greenlandica, Phoco barbata*). They are imported to a considerable extent into this country for the manufacture of a special class of morocco leather. The skins, which are salted, and very oily, are obtained from North America, Newfoundland, the northern parts of Europe, and also from the Cape. They produce a leather which is exceedingly strong and which has an extremely compact texture. A good proportion of japanned and enamelled leather is also made from these skins. The fur-seals of Alaska and the Northern Pacific are sea-bears (*Otaria*). They are dressed for muffs, jackets, caps, and other articles of clothing.

Pig skins are tanned to some extent in Austria-Hungary, and Scotland, and form a very light and tough leather, which is used largely for harness, saddle, and bag work.

Porpoise skins are now much used for boot uppers and for laces, producing when tanned a very soft but strong and tough leather.

Deer skins are tawed and oil-dressed to a considerable extent in the United States, and *alligator and serpent skins* are utilised for the manufacture of fancy leathers for purses, small bags, and similar articles.

CHAPTER V

WATER

There is no material used in the manufacture of leather in such large quantities as water, and it is therefore clear that its quality is a matter of exceeding importance. As the use of pure distilled water is quite out of the question, and as all natural waters contain a certain amount of dissolved matter it is very desirable that the leather manufacturer should consider the nature of the commoner impurities, their influence in the various processes in the manufacture, the methods by which they can be conveniently removed and accurately estimated, and the most suitable sources for the supply of a water of satisfactory quality.

The most common property of natural waters is that of "hardness," a term applied to such waters on account of the difficulty in obtaining a lather in the ordinary process of washing. This property is principally due to the salts of calcium and magnesium which react with the soap and cause the precipitation of the insoluble stearates, oleates, etc., of the same metals. In the water the metals are usually present as carbonates, sulphates and chlorides. The carbonates are kept in solution by the presence of dissolved carbonic acid, which forms soluble bicarbonates with them. When such waters are boiled, however, these bicarbonates are decomposed, carbonic acid is driven off, and the carbonates are precipitated, that of magnesium eventually changing into the hydrate.

$$Ca\,(HCO_3)_2 = Ca\,CO_3 + CO_2 + H_2O.$$
$$Mg\,(HCO_3)_2 = Mg\,(OH)_2 + 2\,CO_2.$$

This expulsion of carbon dioxide and precipitation of chalk and magnesia is the cause of the "furring" of kettles, and its gradual diffusion in nature gives rise to stalactites and other calcareous deposits. Hardness due to the decomposable

bicarbonates of calcium and magnesium is therefore termed *temporary hardness*, whilst that due to the sulphates and chlorides, which is not removed by boiling is called *permanent hardness*. In many industries the presence of these dissolved salts is distinctly undesirable and in many of the processes of leather manufacture may be the cause of decidedly injurious effects; hence many suggestions have been made for "softening" the water by ridding it of these impurities, and outlines of some of the most successful and most widely used of these are now given.

The Clark process, of which a great number of modifications have been suggested, involves the use of a solution of lime. This will remove the temporary hardness only. Calcium hydrate, being a strong alkali neutralises all the free carbonic acid and all that combined as bicarbonate, forming calcium carbonate, which is precipitated; and further, that calcium carbonate which had been kept in solution by this carbon dioxide is also rendered insoluble. The reaction may be expressed thus:—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\,Ca\,CO_3 + 2\,H_2O.$$

Temporary hardness due to magnesium bicarbonate is also removed in a very similar manner, but a further quantity of calcium hydrate is used, the magnesium being removed as hydrate thus:—

$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 = 2\,CaCO_3 + H_2O + Mg(OH)_2.$$

The insolubility of magnesium hydrate causes all the magnesium present as permanent hardness to be precipitated also, but it will be noticed that the permanent hardness is not reduced in this way.

$$Mg\,SO_4 + Ca(OH)_2 = Mg(OH)_2 + Ca\,SO_4.$$

The process as originally carried out consisted merely in mixing the requisite quantity of lime with the water in a vat, and running the mixture into large tanks, to the bottom of which the precipitated chalk and magnesia gradually settle.

The Porter-Clark process is a modification of the above in which some of the water to be softened is used to make

saturated lime water, and so softened in the process, the chalk being deposited with the excess of lime as the solution passes slowly up a vertical cylinder. This lime water is now used to soften more of the hard water by running both of them into another cylinder in the required proportions. An agitator causes thorough mixing and the precipitated calcium carbonate is removed by means of the filter press. This process is arranged so that it may be continuously in operation.

The Archbutt and Deeley process is also a modification of the Clark process in which the object is to shorten the time required for the precipitated chalk to subside and to reduce the space required for settling tanks. In this process the precipitated chalk is not removed but allowed to mix with subsequent charges of water and lime. Steam injectors, at the bottom of the tank cause the mixing of the contents, and also slightly raise the temperature. In this way it is found that the calcium carbonate from previous charges causes a much more rapid settling of that newly precipitated, and is especially helpful when the quantity of magnesia in the water is considerable. It is usual to pass the gases from burning coke into the exit pipe to "carbonate" the softened water, and so render soluble any unsettled carbonate of lime or magnesia, which might otherwise collect in and choke the pipes through which the water passes.

The Caustic soda process, as implied in the name, involves the use of sodium hydrate instead of calcium hydrate. The principle of the process is closely similar to the lime processes, all the free carbonic acid is neutralised, and the dissolved chalk and magnesia precipitated. In this case, however, the carbon dioxide is neutralised to form soluble *sodium* carbonate, which is advantageous in that it causes the removal of some, at any rate, of the permanent hardness of the water, thus :—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

If, however, the permanent hardness is less than the temporary, the softened water will be alkaline with sodium carbonate. The caustic soda solution is run into the hard water at a regulated rate, the temperature is raised by a steam injector, and the mixture passed through the tortuous paths of a conical

mixer, at the bottom and point of which a large part of the sludge rapidly collects and is occasionally run off by opening a cock. The mixture then passes into a settling tank, in which the rest of the precipitate is deposited. This process is also continuous but somewhat costly.

It will be evident that the permanent hardness of waters softened by the lime processes and the permanent hardness in excess of that removed by the caustic soda process can be removed by using in addition to lime and caustic soda the requisite quantity of sodium carbonate. Where desirable, this can usually be arranged to work in with the apparatus used for the softening of temporary hardness only.

The estimation of the hardness of water has been accomplished by titrating with a standard soap solution, the end point being a "permanent lather," but it can now be done much more accurately and scientifically by the methods of Hehner as subsequently modified by Pfeifer and others. Directions for these are now given.

Temporary hardness.—100 cc. of the water is titrated in a hard porcelain basin with N/10 hydrochloric acid and alizarin as indicator. It is necessary to boil off the carbon dioxide continuously, as alizarin is affected by it; this being done, however, the end point, from violet to pale lemon-yellow, is very sharp. With very hard waters the indicator may be precipitated, but this may be overcome by a repetition of the titration in which the indicator is not added until near the end of the titration. Two drops of a $\frac{1}{2}$ per cent. solution of the purest alizarin paste is used.

No. of cc. N/10 HCl $\times$ 5 = parts $CaCO_3$ per 100,000.

Permanent hardness.—200 cc. of water are placed in a clean *Jena* flask and 25 cc. of N/10 caustic soda, and 25 cc. of N/10 sodium carbonate are then added. The mixture is boiled down to about 150 cc. and rinsed with hot distilled water into a 200 cc. flask, cooled, made up to mark, and mixed well. The solution is then filtered, rejecting the first 50 cc. 100 cc. are pipetted from the rest and titrated with N/10 hydrochloric acid and alizarin as before.

(25 — No. of cc. used) $\times$ 5 = parts $CaCO_3$ per 100,000.

If a *minus* quantity is obtained there is no permanent hardness, and the water contains sodium carbonate, which being thus estimated, should be deducted from the temporary hardness. Each part so deducted corresponds to 1·06 parts of anhydrous sodium carbonate.

Magnesia hardness (whether temporary or permanent).—100 cc. of the water are titrated to neutrality as in the determination of temporary hardness. 25 cc. of lime water (50 cc. if the quantity of magnesium is great) is placed into a 200 cc. flask with a long stoppered neck and the neutralised water run into it *hot*, rinsing the basin with hot carbonic acid-free distilled water. The mixture is mixed well, warmed for a short time on the water-bath, cooled, and made up to mark. It is now filtered, the first 50 cc. being rejected, and 100 cc. titrated with N/10 hydrochloric acid and phenol phthalein, in the cold. The process is repeated exactly with distilled water instead of the water being analysed. It being supposed that x cc. of N/10 acid were used for the first titration and y cc. for the second,

$$5(y - x) = \text{magnesia hardness in parts } CaCO_3 \text{ per } 100{,}000.$$

In any of these calculations "parts $CaCO_3$" may, of course, be readily converted into "parts" of Ca, CaO, Mg, MgO, etc., by factors obtained from the atomic weights.

Lime required for softening will include any free carbon dioxide over and above that combined as bicarbonates, and may be determined by repeating the process for the determination of magnesia hardness with the unneutralised and unboiled water. Actual free carbonic acid can be estimated by titration of 100 cc. of the water with N/10 caustic soda and phenol phthalein.

Other than these, the chief constituents of the water which it is desirable to estimate are chlorides, iron, and nitrogenous matter. Chlorides are easily determined by titrating 100 cc. of the water with N/10 silver nitrate and the chromate indicator, and iron can be readily determined colorimetrically with thiocyanate. Nitrogen is best determined by the Kjeldahl process (p. 398), and is important as indicating a possible contamination with sewage, and consequent bacterial infection.

There is no doubt whatever that for the purposes of the leather manufacturer the best water is that which is most free from dissolved matter, both inorganic and organic, and it may be useful to note here the effect of some of the usual impurities on the various processes of the manufacture. In soaking hardness is of little moment, the most important matter being the freedom of the water from bacteria, which would have a solvent or other injurious effect on the hide or skin. In liming all temporary hardness is removed in making up the liquor, and any permanent hardness in the form of the sulphates of calcium and magnesium will help in plumping, though chlorides are said to act in the opposite direction. Any sodium carbonate, either naturally occurring or from the caustic soda softening process, will be converted into hydrate and assist in the operation. Injurious bacteria may also make their influence felt here, though the lime acts as an antiseptic to many of them. In the unhairer's and flesher's water pits the occurrence of any dissolved carbonates in the water is exceedingly injurious, for they interact with the caustic lime on the hides or skins and cause the precipitation of calcium carbonate which roughens the grain and which is not removed by the weak acids in any of the various deliming processes. This carbonate will also cause discolorations in the liquors (see below). Temporarily hard waters are exceedingly bad in this respect, for they not only fix the carbonate formed from the lime and carbonic acid, but also that contained in the water itself. The addition of a slight excess of lime to these pits is very desirable, for acids do not satisfactorily expel the carbonic acid they liberate. Water containing sodium carbonate may cause this effect also, which may be remedied as indicated above or by the addition of a slight excess of calcium sulphate. In either case a thorough mixing is necessary. In the deliming processes the same remarks are relevant, but the freedom from bacterial contamination is even more important. In leaching temporary hardness is very objectionable, for the metals combine with many times their own weight of tannin, making it quite useless by the formation of insoluble tannates, and, furthermore, these are readily oxidised to dark-coloured compounds and are a very common cause of discolorations

and stains on tanned goods. The same objection applies with equal weight to the dissolving up of extracts. In these cases the difficulty can be got over quite satisfactorily by the use of oxalic acid, which precipitates the calcium entirely from solution as oxalate, or by the addition of sulphuric acid, which converts the temporary hardness into permanent, this latter being much less injurious in this way as the calcium is combined with a strong acid, and will therefore not react readily with the tannic acids. The introduction of iron into any of the processes will also result in the appearance of marks and stains of a very similar nature.

The occurrence of appreciable quantities of chlorides in the liquors is also objectionable for sole leather tanning, as these have considerable power in preventing "plumping." In the mineral tannages hardness is of much less consequence, but in fat liquoring (p. 356) each part of hardness causes the destruction of more than twelve parts of soap by the precipitation of insoluble lime and magnesia soaps, which are also liable to stick to the leather and make trouble in the finishing processes. A very similar difficulty occurs in scouring. In dyeing, iron must be absent, and temporary hardness is injurious in that it reacts with and precipitates the basic dyes, and may cause unevenness of colour by the deposit of this precipitate. This difficulty does not arise with the acid dyes, and may be overcome in the former case by addition of acetic acid.

For boiler purposes all hardness is very undesirable. Temporary hardness, as we have seen, is destroyed by boiling, but this involves the precipitation of the dissolved carbonate as a "sludge," which it is necessary to remove at intervals. Calcium sulphate is also insoluble in water at high temperatures, and is deposited as a very hard scale, whilst magnesium chloride hydrolyses, and the liberated hydrochloric acid may cause corrosion. Only mineral oils should be used for cylinder purposes, as those of animal or vegetable origin form sticky deposits of lime soaps which are very apt to cause the plates to be heated unevenly. A properly softened water, moreover, is much better than any boiler compositions.

From these considerations it is clear that the purer the water

supply is the better are the results obtained by it. The best natural water is rain water, and where there is no other good supply it is strongly advisable to make some attempt to collect this and use it at least for the leaches and liquors. River water ranks next, whilst well water is often exceedingly hard.

CHAPTER VI

SOAKING

The process of soaking is essentially one of softening and cleansing by means of water. As we have already noted (p. 17), both gelatine and hide substance are practically insoluble in water, though water is absorbed by them, so that there is no danger of the loss of our gelatinous raw material through a solvent action unless water at a high temperature be used. On the other hand the albuminous matters, such as the blood of the minute corium vessels, as well as that which has been allowed to adhere mechanically to the exterior, and the lymph, are soluble in water and are dissolved by it in the soaking process. Dung is also softened by the water and ceases to adhere to the hide or skin. It is desirable to remove both blood and dung because they are both liable to cause the appearance of stains in the later stages of the manufacture, and the latter is apt to counteract the plumping influence of the limes by acting as a mild bate. If therefore after the soaking process any dung still adheres to the hide, it should be mechanically removed by some blunt instrument before the goods enter the lime liquors. Earthy matters are also removed by soaking, and the possibility of "iron stains" from this source thereby eliminated. It is also necessary in the case of cured hides to remove salt and other materials which have acted as preservatives, and as these usually are readily soluble, this also is accomplished by soaking. Even for wet salted hides a considerable dehydration of the original skin material has occurred, and it is one of the functions of soaking to restore this moisture to the hide and to bring it back again into the condition in which it was before the cure was effected. All these operations are most efficiently accomplished by the plentiful use of water.

Bacterial action.—For sole and heavy leathers it is highly desirable to accomplish these objects without putrefaction and consequent loss of truly gelatinous matter, and hence it is exceedingly important that the possibility of bacterial action should be reduced to a minimum. In the case of some of the lighter leathers, however, this is less important, for in these a partial peptonisation and loss of the gelatinous fibre cementing substance may even be desirable in order to produce the requisite pliability and softness. In bacterial action, however, the difficulty is to obtain that kind of decomposition which is desired, for indiscriminate putrefaction undoubtedly leads to ruin, and there is as yet little definite knowledge as to which are the ferments which will bring about the desired effect, and which are the organisms which attack the grain and more valuable portions of the hide or skin. There are a few defects, such as "stippen" (spots) "weak grain," etc., which have been identified as originating in the soak liquors, but as many of these injuries only become noticeable in the tanned or finished leather the matter is difficult to investigate. If these influences were less obscure, the hide might be introduced into an appropriate sterile medium and a pure culture of the desired bacteria added, but all that can be done as yet is to keep the putrefaction within limits, and by empirically discovered arrangements to encourage that bacterial influence which has been found to produce the desired effect. In the case of dried and dry-salted hides in which the difficulty of softening is much greater, it was once thought essential to allow a certain degree of putrefaction in order to produce the required softness, and "putrid soaks" were therefore used for this purpose, but it is now universally recognised that this is both undesirable and unnecessary; the danger of "damaged grain" due to uneven attack, the risk of extensive loss of pelt substance, by action at an irregular rate, and the very careful supervision always required for the process, all contributing to its overthrow.

Mechanical treatment has been resorted to for assistance in both the softening and cleansing processes. It was once not uncommon to give hides, after some preliminary soaking, a "breaking over" by means of a blunt tool on the beam,

which operation also assisted in the removal of the dung and dirt, and this process is still employed for some skins. The "fulling stocks" (Fig. 15) have also been very popular for

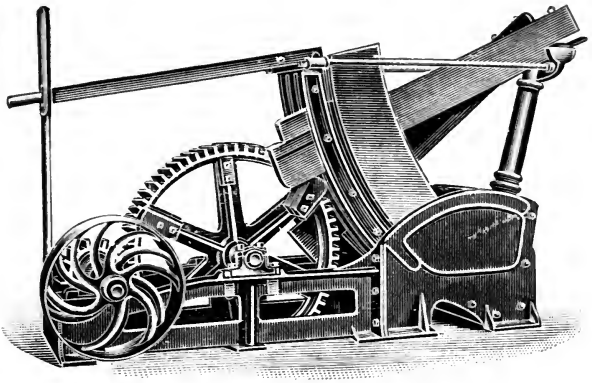


FIG. 15.—Stocks (Farrar and Young).

dried and dry-salted hides and skins. These consist of two heavy hammers, raised alternately by projections on a revolving wheel, and allowed to fall on the hides which are contained in a curved box below. This beating or kneading

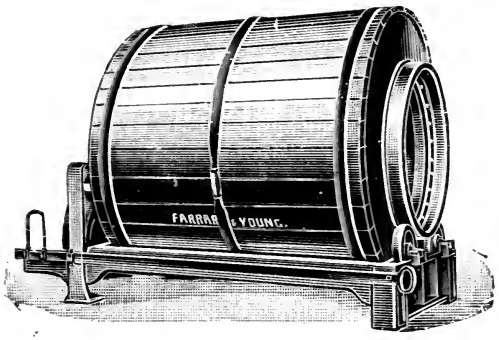


FIG. 16.—Scotch tumbler

action is continued for rather less than half an hour, according to the quality and condition of the material, and is used only to assist in the softening by water. The American "hide mill" is a modification of this arrangement, and "crank

stocks" have been found useful for the smaller hides and skins. The possibilities of mechanical damage and of the unnecessary loss of hide substance, however, have been increasingly recognised, and these rather severe methods of treatment are now much less generally used.

"Drums" or "tumblers" are now considered to give an efficient and safe mechanical action, and their use is very widely extended. There are many forms of these, but they are all large wooden cylinders capable of slow rotation about their axis. One common form, shown in (Fig. 16), is fitted in the interior with shelves or blunt pegs, as in the

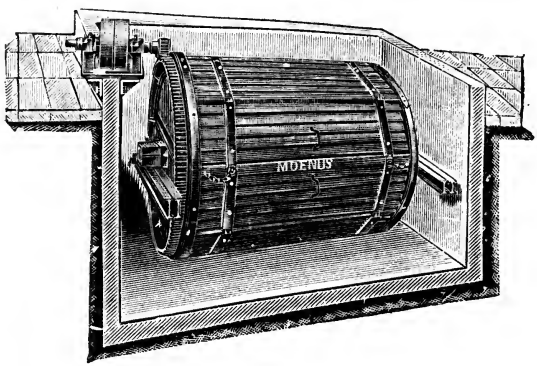


Fig. 17.—Latticed drum

common churn. The goods are inserted through the hole in the side and a continuous stream of water may be run in during the operation, an exit being arranged by pulling a plug in the front of the drum. The direction of rotation is usually reversible. These drums are also employed for tanning, dyeing, and other operations. Another useful form consists merely in a staved cylindrical enclosure which rotates in a deep tray of water. A "lid" or opening is arranged in the staved part of the drum (Fig. 17). Like the stocks, these are chiefly used to assist in the ordinary pit soaking, and are useful at all stages, according to the class of goods.

Chemical assistance is also extensively employed, the aim being to use a substance which will not only assist in softening and swelling but will also have some antiseptic action, and at

the same time have no solvent or injurious effect on the hide substance and cause no complications when the hides are transferred to the lime liquors. Dilute mineral acids, which have considerable antiseptic effect, have been tried, but their swelling effect is rather drastic, and it is generally necessary to neutralise them before the goods are forwarded to the limes. Of these a 2 per cent. solution of sulphurous acid has been found to give the best results, ammonia or sodium hydrate being used to neutralise. Borax, boric acid, sodium carbonate, ammonia, salt, potassium nitrate, arsenic sulphide, and many other substances have also been suggested, their action being generally that of a mild antiseptic, and also in the case of the acid and alkaline substances, that of a weak swelling agent. They all seem open to some objection, however, and as some are rather costly, it is not surprising that they have never been widely adopted. A 0·1 per cent. solution of carbolic acid is excellent if it is desired to make or keep the soak liquor quite sterile, and the only objections to its use are that it tends to coagulate albuminous matter, and that it is liable to carry its antiseptic effect into the limes and so render the process of depilation decidedly slower. It is very useful however, for tainted goods as a preventive of further damage. Practically all that is desired in a chemical assistant to the soaking process is found in the use of a 0·1 per cent. solution of caustic soda. A solution of this concentration has very considerable softening and swelling effect, and acts rapidly on the most obstinate hides. It is a reagent which it is not necessary to neutralise or remove and which causes no complications when the goods enter the lime liquors, being in fact often one of the constituents of these. Its solvent effect on hide substance is very small and at this concentration has been shown to be practically *nil*; and whilst it is a fairly good antiseptic to all common putrefactive organisms, it is not so fatal to those which are useful in the unhairing process. A 0·2 per cent. solution of sodium sulphide has been also found to give good results, but the time required by it is rather longer, and its solvent effect is slightly greater. Both are now extensively employed for this purpose and there is much to be said for them also from a sanitary standpoint.

The nature of the treatment which should be applied in practice naturally varies very widely with the class of goods and their condition when received. No hard and fast rules can therefore be given, but some idea can be gathered as to the extent to which this operation is desirable from the following outline of the methods used for the commoner classes of goods.

Market hides, which are uncured and not dehydrated, require chiefly the cleansing effect, being already in a fairly soft and moist condition. The chief aim in this case should be to reduce the time of soaking as far as possible; and two fresh waters, in each of which the goods only remain a few hours, are all that are usually required, though a third water may be occasionally desirable. For "slippy" or even slightly tainted goods the use of the tumbler is necessary as a preliminary operation, with possibly the addition of carbolic acid. If a drum is not available the first water should be changed in about four hours. The use of the drum is also desirable in hot weather. It is not uncommon to use a weak lime liquor as a soak water for green hides.

Salted hides require a decidedly longer soaking, for in this case a certain amount of dehydration has occurred, and hence some softening and swelling are necessary. It is also very desirable to get rid of the salt as far as possible, for if not the hides are said not to plump satisfactorily in the limes. Besides this flattening action it is to be borne in mind that common salt in 10 per cent. solution has a distinct solvent effect on the hide fibre, and as this concentration is soon reached with salted goods it is necessary to change the goods very quickly from the first water and fairly soon also from the second. It should be remembered that salt has a checking influence on bacterial growth and action so that a more prolonged soaking is admissible without sterilisation. At the very least three waters should be given, some American yards giving much more, and in any case it is decidedly advantageous to remove the last traces of salt by means of the tumbler and running water. No other mechanical treatment is necessary with such goods. It is permissible for these soaks to use the third water of one pack as the first water of a new pack, and some economy of water is thereby effected.

Dried hides and dry-salted hides are naturally softened with much greater difficulty than are wet-salted goods, and with regard to the removal of salt the remarks just made still hold good. In these cases it is often necessary to extend the soaking to a week or more. Dried hides can be left for a considerable time in their first water if carbolic acid or borax be used, but dry-salted hides should be changed more quickly on account of the solvent action of the salt. Drumming with slightly warmed water may occasionally be helpful after some preliminary soaking in the cold, but this is dangerous for goods which are not quite reliably sound, for then the bacterial damage would proceed further, unless antiseptics were added. Some tumbling in cold water is desirable in any case, but the use of "putrid soaks," stocks, and other drastic measures is to be condemned for regular use. It is for this class of goods that the use of caustic soda and sodium sulphide has been the greatest boon. With these, dry hides can be satisfactorily softened in one or two days, a short soak in fresh water or a slight drumming in running water being all that is further necessary.

E. I. kips are treated much in the same way as ordinary dry-salted hides. It used to be common to give them a short soak and then put them in the stocks, but it is usual now to use chemical assistance. They are soaked over night, and next morning hauled, and swilled to remove the "cure." They are then placed in a sodium sulphide soak till next day, and finished by drumming in running water till soft. Flint dried kips may be given about a week's soaking in a water made sterile with carbolic acid.

Calf skins are usually uncured, but should receive three short soaks in fresh water. If salted, further treatment is necessary.

Goat skins, if salted, should soak over night and then be stretched, after which they should be soaked for a few hours in a fresh water and drummed. After further soaking they are worked over the beam. The treatment should be continued until the skins are thoroughly soft, and antiseptics used if the process be prolonged. Flint dried goods should have a rather longer preliminary soaking, and the second water should

contain sodium sulphide or borax, the whole operation in this case taking about a week.

Seal skins are treated with warm water (about 25° C.) to assist in removing the large quantity of oil they contain. After cooling in this water they are "blubbered" or "brushed over" with a blunt knife on both sides, and the oil thus eliminated. This treatment may be repeated, with perhaps some drumming, until ready for the limes.

As a rule the time required for soaking skins is less on account of the thinner character of the goods. It is a good maxim both from a bacterial and chemical point of view to make the first soak the shortest, and it is highly necessary that soak pits should be effectively disinfected at definite intervals. For this purpose "creolin," which is a tar oil containing phenols and cresols emulsified by soap, is very efficient, though carbolic acid alone is quite satisfactory. Another point to bear in mind is the undesirability of making up the last soak water of any pack in a pit which has just been used for a first water, unless the pit has been disinfected or cleaned.

The chemical control of this process involves principally the determination of the nitrogenous matter which goes into solution. This can readily be determined, when necessary, by Kjeldahling. The nitrogen found includes that from ammonium salts, albuminous matter, and peptonised hide substance, but it is often convenient to state this result in terms of undecomposed hide substance, on the assumption that it contains 17·8 per cent. of nitrogen. Where caustic soda is used it can be easily estimated by titration in the cold with N/10 acid and phenol phthalein. The ammonia may render this result slightly inaccurate, but for control work all that is necessary is to keep the alkalinity approximately constant, and by this method a caustic soda soak can be repeatedly used for dried hides, but for dry-salted goods the rapid accumulation of salt must be considered. Salt can be estimated as in water analysis, the solution being first made neutral by the addition of a slight excess of formic acid and subsequent addition of magnesia.

CHAPTER VII

UNHAIRING

The term **unhairing** or **depilation** is usually understood to include not only the mechanical removal of the loosened hair of hides and skins, but also the means by which they are brought into a suitable condition for such treatment, and also those other trimming and cleansing processes which are associated with this operation in practice. Depilation is brought about either by "sweating" or by "liming." In sweating the hides or skins are subjected to a regulated putrefactive process, which is stopped when the hair is sufficiently loosened to be removed by gentle mechanical treatment. In liming the hides or skins are immersed in milk of lime, occasionally assisted by other depilatants, and the hair and other epidermal structures similarly attacked. The lime also swells the corium fibres, and at the same time saponifies or emulsifies the greasy matters of the skin.

Depilation by Sweating.—This is the most ancient method of removing hair, and was first accomplished by merely piling the skins in a heap and allowing them to putrefy. Later it was discovered that the principal factors which controlled this fermentive action were the temperature and humidity of the surroundings, and hence it is now general to conduct the process in closed chambers in which these forces are within control. A series of such chambers together form the "sweat pit."

The cold-sweat system is carried out largely in the United States of America for unhairing the thoroughly softened flint hides. The sweat pit is a structure which may be entirely above ground, and is built of stone and is protected from outside climatic influences by another wall and a lining of timber, earth, tan bark, etc. A passage about 7 feet wide runs between two sets of chambers, which have each tight

doors, ventilators, and windows. The pit is covered with a false bottom, under which are the pipes that deliver the steam for warming and moistening the atmosphere. By means of a cold water sprinkler also the temperature is kept between 60°—70° F. The hides are hung on hooks, and each chamber takes a pack. The sweating lasts usually four to five days, and, especially near the end, is very carefully watched by experienced men. When complete, the hides are thrown into either water or a weak lime liquor, which takes away the "slimy" feel and produces a slight swelling, so that the hair can now be conveniently scraped off with a blunt knife.

The warm-sweat system is employed largely on the Continent both for hides and for sheep skins, in which latter case it is often termed "staling." The process is very closely similar to that just described, but takes place at a higher temperature (75°—80° F.) and is on the whole rather quicker. In this process the putrefaction makes rapid progress, and the operation requires even more care than that just described. A slight salting on the flesh side is occasionally practised.

Both these processes are attended with very grave risks of injury through the bacterial action going too far or being uneven, and it is very common to find leathers with damaged grain when the goods have been unhaired by this method. The putrefactive bacteria attack first the hair root and epidermal structures, but afterwards will also attack the corium, and there is a further risk that some injurious bacterium may thrive under the conditions used. A considerable quantity of ammonia is produced by the ferments as a decomposition product, and this doubtless affords considerable assistance in loosening the hair. Procter, indeed, has shown that a sterile ammoniacal atmosphere will produce a similar effect. Further disadvantages of sweating are that grease is not "killed" as with lime, and there is little, if any, swelling, so that it is necessary to "raise" the pelt by subsequent liming or by treatment with acids before commencing the tannage.

Depilation by Lime.—The use of milk of lime for unhairing dates back many centuries, and the effects that it is capable of producing under varying conditions have therefore been long

known through the extensive experience and empirical observations of unscientific men. Although its mode of operation is now very much more clearly understood the whole process of depilation involves so many different actions that it has been difficult to find a material which will yield the same combined effect, and hence the principal modifications which have been introduced consist usually in using some other material in addition to lime and in that way assisting its influence in the required direction. Lime, at any rate, has the great advantage that it is a common and cheap material. It is obtained from natural limestone and chalk by "burning" with coal in a kiln. In this way the calcium carbonate, which forms the principal part of these substances, is converted into calcium oxide by the elimination of carbon dioxide from the molecule.

$$CaCO_3 = CaO + CO_2.$$

The reaction may be represented by the given equation, but the process is really more complex, and a good proportion of carbon monoxide escapes with the furnace gases.

Quicklime, or calcium oxide, is a white, amorphous, and infusible solid which possesses a very strong affinity for water, and which is therefore useful in many cases as a dehydrating agent. When a small quantity of water is poured upon it combination takes place with the evolution of a considerable amount of heat, some steam is evolved, and the mass swells to some extent and crumbles to a soft and apparently dry powder. This operation is known as the "slaking" of quicklime, and results in the production of "slaked lime," or calcium hydrate.

$$CaO + H_2O = Ca(OH)_2.$$

Ordinary quicklime is, however, very liable to contain magnesia as well as various silicates, and if the heating in the kiln has been too intense these latter substances fuse and cause the quicklime to have a much more compact texture. The lime is then said to be "dead burnt," and is found to slake with much greater difficulty. Heat is a considerable help to slaking, and by adding only a small quantity of water to the lime the heat evolved is utilised in assisting the reaction. If a large quantity of water is added this heat is merely used in

slightly warming the water so that both the reaction and the disintegration would proceed much more slowly. This should be remembered in making up the lime liquors. Calcium hydrate is soluble in water to the extent of one part in 778 parts water, but this varies slightly with the origin of the lime and the nature and extent of its impurities. It will be seen, however, that its solubility is very limited, its saturated solution being about N/20, and from the standpoint of the

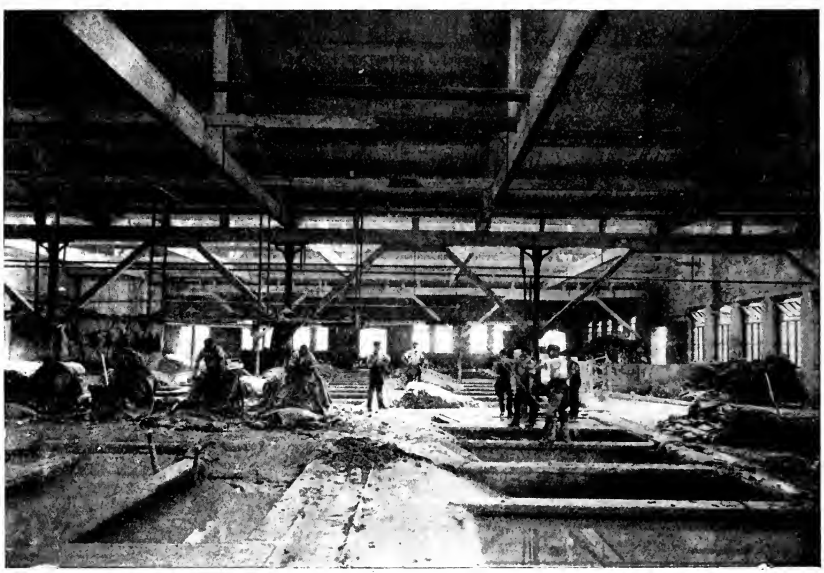


FIG. 18.—Lime Yard (Messrs. Walker, Ltd., Litherland).

leather manufacturer this is an advantage, for even if a saturated solution be used it is only a comparatively mild reagent, and some variation in the time in which it is in contact with the goods makes, therefore, very little difference, and as it is usual to use it at its full strength the exact quantity to add does not seriously matter so long as there is an excess of undissolved hydrate. For the same reason, moreover, it is almost impossible to ruin goods by the accidental employment of too large a quantity, and all these are

no doubt further reasons for its continued popularity. As a considerable amount of hydrate is absorbed by hides and skins when they are in the lime liquors, it is indeed necessary to have some excess of undissolved lime to take the place of this, and hence it is quite general to use "milk of lime" rather than "lime water" for the lime liquors of the unhairing process. The lime may be kept in the yard in the form of oxide and the liquors made up by allowing the proper quantity to slake over night in the bottom of the lime pit and then making up the liquor by adding water and mixing well, or a large quantity of lime may be slaked in a shallow tank and afterwards mixing to a stiff paste and thus used as the source of supply for making up the liquors. It should never be tipped into the liquors in unslaked lumps, for this leads to local heating and the burning of the goods.

The mode of action of the lime is entirely chemical, and takes place in several directions. Being a caustic alkali it attacks the softer keratinous structures of the hide (*rete malpighi*, hair bulb, etc.), first softening and finally dissolving them; but on the harder keratins it has practically no effect, so that the hair is little damaged by the ordinary lime liquor. This solvent action is the basis of the unhairing property of the reagent, for on the gelatinous hide fibre it has little solvent effect. It has, however, a vigorous physico-chemical action on the corium tissue, by which water and lime are absorbed by the hide in considerable quantity. This change may be distinctly separated into two distinct parts, swelling and plumping. *Swelling* may be defined as the extent to which the surrounding solutions is absorbed by the hide fibre and it can be measured by the increase in weight. This has been shown to be a function of the concentration of the hydroxyl ions of the solution,[1] and is therefore obtained with other alkalies and is increased by the use of more strongly ionised solutions. It is, however, not directly proportional to this factor, but is influenced by the basic radicle from which the OH ions have dissociated. The *plumping* effect is the change by which the soft and flacid hide becomes firm and elastic. Both these actions are fairly vigorous with lime, but other

[1] Stiasny, *see* Collegium, 1907, 128.

alkalies produce very different effects. Both ammonia and caustic soda will swell, but the ammonia-swollen hide will always be soft and unplumped, whilst the soda-swollen hide will be violently plumped. Baryta, like lime, is intermediate in both effects. The function of this physical change in the hides is to separate the fibres and to split them up into the finer fibrils of which they are composed. This separation is very helpful in rendering the tanning process both quicker and more complete. A certain small amount of the interfibrillar substance is also dissolved by the alkali and a certain amount of lime "fixed" in the fibres so that it is neutral to phenol phthalein but not to methyl orange. Lime also acts upon the natural fatty and oily matters of the skin and converts them into insoluble calcium soaps which are removed partly in unhairing and partly in scudding.

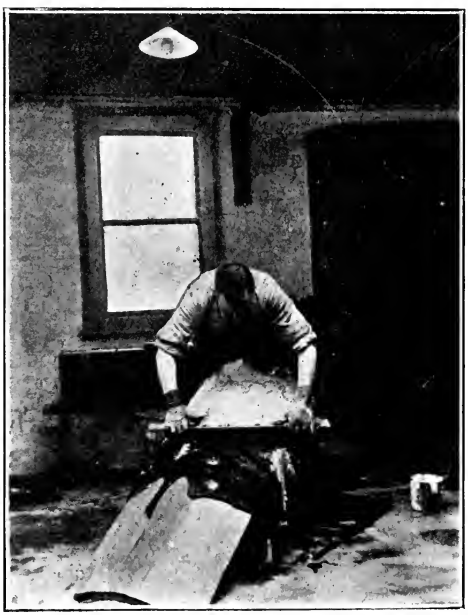


Fig. 19.—Unhairing by hand labour.

Sodium sulphide, Na_2S, 9 H_2O is now used to a considerable extent as a depilatory agent. It may be obtained in pale brown deliquescent crystals which contain only about 30 per cent. of the actual sulphide. In solution it decomposes into NaOH and NaSH and it is to both these substances that it owes its characteristic effects. It rapidly attacks and dissolves keratinous matters, but the gelatinous tissue is much less affected by it and hence it was first used for unhairing by painting the hair side with a strong solution, the hair and epidermis being rapidly reduced to a pulp.

The disadvantages of the process were that the hair roots were not removed in this way and the hair was a total loss, and as, moreover, the sulphide is expensive when compared with lime it was necessary to make some modification in the method of treatment. It is now common to mix lime with its solution and paint the *flesh* side of certain skins with the mixture. In this way the hair root is attacked first and when softened the hair can be pulled away quite uninjured. It is also added in smaller quantities to the ordinary lime liquors, especially during the short hair season, and so assists in rapid and complete unhairing.

Arsenic sulphide,[1] realgar As_2S_2 has been used as an assistant to lime for many years. It is found in nature but is now prepared on a large scale by distilling a mixture of iron and arsenical pyrites. It is a red solid, which is insoluble in water, and hence cannot be added directly to lime liquors. It is added to slaking lime, a complex chemical action then taking place, in which **calcium sulphydrate** $Ca(SH)_2$ and a little calcium sulpharsenite are formed. It is the former of these which produces the characteristic action of an arsenical lime, and the quantity which is formed depends upon the temperature reached in slaking and the proportion of realgar mixed with the lime. The higher the temperature, the more powerful is the product. It will be noticed that in this case no caustic soda is produced, and it is this fact which constitutes the difference between a lime liquor made up with realgar and one made up with sodium sulphide. Calcium sulphydrate with excess of lime has a solvent effect on the keratins as great as sodium sulphide, in equivalent quantity, and it has been shown by Stiasny that the solvent action is due to the joint action of the OH and SH ions, and is at a maximum when they are present in equal proportions, as it is found in the solution of sodium sulphide.

Many suggestions have been made to obtain calcium sulphydrate and the effects it produces in other ways. "Gas lime," which contained the sulphydrate and sulphide of lime, was once used to make a paint for unwooling lamb skins. The "tank waste" of the Leblanc process consists chiefly of calcium

[1] Quite distinct from the yellow As_2S_3 and As_2S_5, which, however, may be employed quite similarly.

sulphide; but by the action of atmospherical moisture sulphydrate is formed, and the product has been used for unhairing. A very similar mixture was patented by Lufkin, who mixed sulphur with soda ash and added the mixture to slaking lime.

Caustic soda, sodium hydrate, NaOH, is also used to "sharpen" the action of lime for certain classes of goods. It may be added directly to the lime liquor or produced there by the addition of carbonate of soda. The addition of "wood ashes," which are chiefly potassium carbonate, will, of course, produce a similar effect and has been long practised. Caustic soda is used on the Pullman-Payne process to produce lime in the skin by first using a bath of caustic soda and afterwards one of calcium chloride. It forms soluble soaps with the greasy matters of the skin and both swells and plumps the hide fibre with great vigour.

FIG. 20.—Fleshing by hand labour.

Bacterial action is nearly always a prominent factor in the unhairing process and indeed it is a question whether, with some materials, the ordinary depilatory effect can be obtained without its aid. Although a new lime liquor is an almost completely sterile medium, the solvent effect it exerts on the various proteid matters which enter it causes the amount of organic matter which is in solution gradually to increase. In this way it is made possible for certain bacteria to thrive and then also assist in dissolving further quantities of both keratinous and gelatinous matter. If, therefore, a liquor be

repeatedly used, it is clear that there will be not only a rapid accumulation of both the hydrolytic and putrefactive decomposition products of the proteids (ammonia, amines, salts of amido acids, peptones, etc.), but also an almost proportionate multiplication of the fermentive organisms; and it is evident that if this be continued indefinitely the liquid may continue to unhair, but it will be by virtue of its bacterial rather than its chemical activity.

It has been long thought that the ammonia formed in lime liquors by bacterial action was a powerful assistant in loosening the epidermal structures by its solvent effect, and this was apparently borne out by the rapid loosening of the hair which occurs when pieces of hide are placed in weak ammonia solutions. Stiasny, however, has shown that in an old lime liquor the ammonia forms complex compounds with the calcium salts present, of which the familiar $Ca(8\,NH_3)\,Cl_2$ may be regarded as a type, and that under these circumstances no unhairing effect is produced. The depilatory and solvent effects of old lime liquors therefore are due almost entirely to bacterial action and are prevented by the addition of antiseptics.

From the above considerations, therefore, it is possible to judge the effect that various liquors will produce. An old or "mellow" lime liquor, by virtue of its bacterial activity and solvent effect not only on the keratins but also on the gelatinous and interfibrillar substances, will tend to produce a leather which is soft or loose, and with a dull grain. It will unhair quickly from the same cause, but will not plump, on account of the ammonia present. A new lime liquor, especially if sharpened by the presence of caustic soda, will be pretty strongly antiseptic and have little solvent effect on the gelatinous matters, whereas the swelling and plumping effects will both be strong. With caustic soda, however, there is a tendency towards a rough grained leather. If arsenic sulphide has been used the purely depilatory effect is greatly assisted, and if slightly mellow the moderate amount of bacterial action will assist in producing a soft and flexible leather, but with a sound and silky grain. With sodium sulphide the unhairing is quickened, the plumping effect better, but the resulting

leather may be rather harsh grained unless the sulphide is present in small quantity. If an old sulphide liquor be used a certain amount of pliability may be thereby introduced. In this way it is possible to determine what liquors are most suitable for the class of leather we desire to make. In **sole leather** manufacture where weight and firmness are important, it is clear that a short liming in new liquors is very desirable to keep the solvent and fermentive actions at a minimum; and that caustic soda may be beneficial in order to get the full plumping effect. A significant fact, pointed out by Eitner,[1] is that although the solvent effect of an old lime liquor is in the long run much greater than that of a new lime, it is decidedly less during the first two days of contact. Hence it is wise to place the hides first in the oldest lime to get the softening and partial swelling effect, and least solvent action; and afterwards into a newer lime where the solvent effect will then be least and the plumping effect at a maximum. This has long been a common mode of procedure. With **harness and belting leathers** a greater flexibility is required and hence it is desirable to have rather more mellow liquors; though it is possible to produce nearly the same effect by liming as for sole leather, with perhaps a little sodium sulphide, and allowing the solvent bacterial action to take place in the "bating." For **upper leathers** a somewhat long and mellow liming is desirable (as well as bating) in order to obtain the requisite "feel." For the **light leathers** where softness and pliability are important, a long mellow liming is desirable, and for "glove kid," etc., where a glossy grain is required, the use of arsenic sulphide is an advantage.

The Mechanical Operations of the Lime-yard.—The liming of the hides and skins is usually carried out in pits of which the sides are built of masonry and the tops are level with the floor of the yard. They will usually take a "pack" of several dozen hides at once, or a proportionate quantity of skins. When the liquor is made the milk of lime is well "plunged" up with long poles, and the hides laid in horizontally one at once, pressing each one down with poles to ensure

[1] Der Gerber, 1895, 157 and 169.

proper immersion. After remaining thus for the particular period required they are "hauled" up again by means of poles to which a blunt hook is attached, and piled one above the other

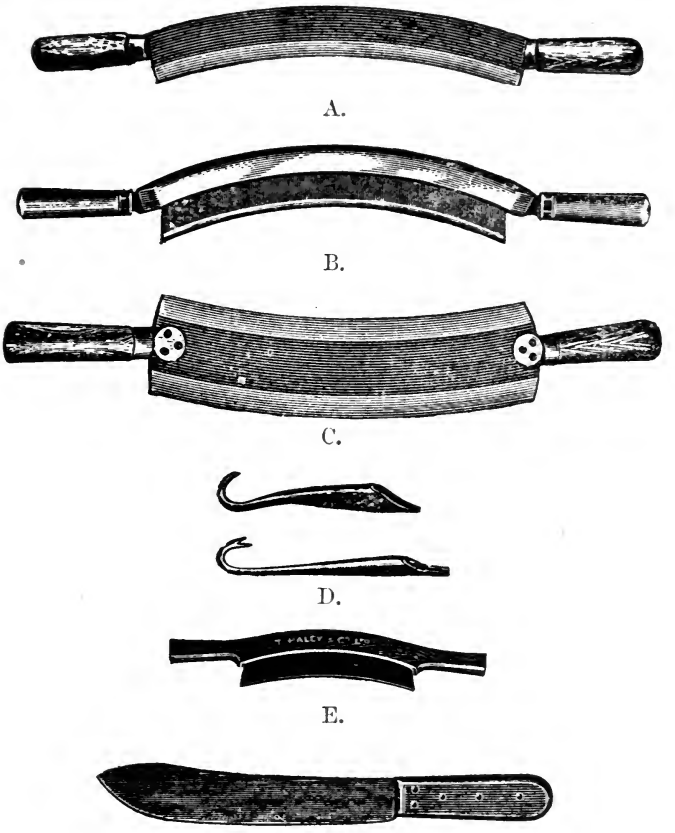


FIG. 21.—Beamhouse tools.

A, unhairing knife; B, scudding knife; C, fleshing knife; D, hauling hooks; E, scudding slate; F, rounding knife.

until either that pit or another has been plunged up and prepared to receive the pack. On coming from the last liquor they are taken by the "unhairers," and laid over a sloping wooden "beam," which has a convex surface covered with

zinc. The hair is then removed by scraping with a blunt "unhairing knife," the motion being away from the operator. The hides are then immediately thrown into soft water, from which they are taken by the "fleshers" as required. These workmen lay the hides again over the beam, flesh-side up, and by means of a sharp "fleshing knife" cut off the pieces of adhering flesh, fat, tissue, etc. They are then thrown into water again to preserve them from the carbonation of the

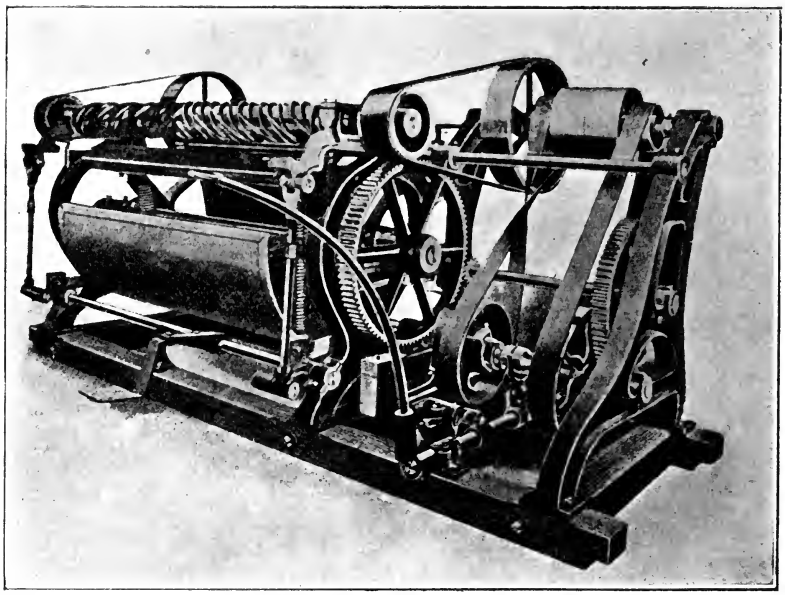


FIG. 22.—Drum beam-house machine.

caustic lime on the grain by atmospheric carbon dioxide. Hides then go to the rounding table[1] and are cut up as explained earlier (p. 32), and are then ready for the deliming process. Skins are not rounded, but both hides and skins may for certain purposes be "split" at this stage by machine to form "grains" and "fleshes" of equal area, which may afterwards be tanned in very different ways.

[1] In America and sometimes in this country they are cut down the back into "sides."

The use of machinery for the beam-house work is also gradually increasing, and slowly superseding hand labour. These machines are usually cumbersome, expensive, and require a good deal of power, but are constanly being improved and made more suitable to the conditions required for the treatment of any particular class of goods.

Unhairing machines are the least satisfactory beam-house machines, and are gaining ground very slowly on hand labour for various reasons. Unhairing by hand is not difficult work and can be done at considerable speed by practised men, and

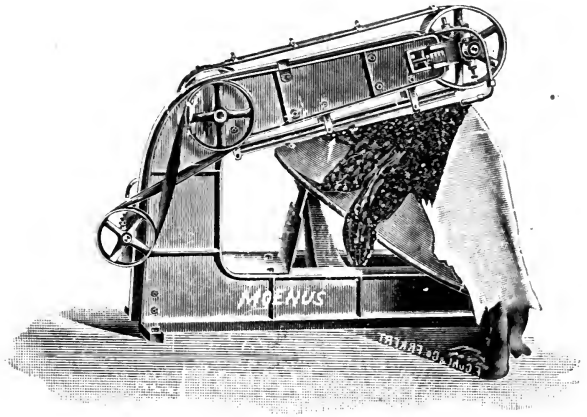


FIG. 23.—The Conus unhairing machine.

it is also a much cleaner process, for most goods unhaired by machines need to be gone over by hand, especially at the edges, after passing thorough the machine. Goods unhaired by hand are, moreover, much less liable to damage in the process, because the pressure that is applied can be varied as necessary on different parts of the hide.

The *Drum* beam-house machine (Fig. 22), sometimes known as the "Vaughn" machine, but now made by the Turner Co., Ltd., represents one type of unhairing machine. The working tool is a cylindrical roll with spiral knife blades. These spiral blades vary considerably in sharpness of edge and steepness of pitch, according to the class of goods for which they are

intended, and are generally arranged to be left-handed in one half and right-handed in the other half, hence scraping the goods both sideways and in the direction of rotation. Another feature of the machine is the semicylindrical drum, covered with thick rubber, over which the goods are placed, half only on the outside. When this rotates the clamped hide is drawn under the spiral blade; the motion of the drum then automatically reverses and the roll rotates at a much higher speed.

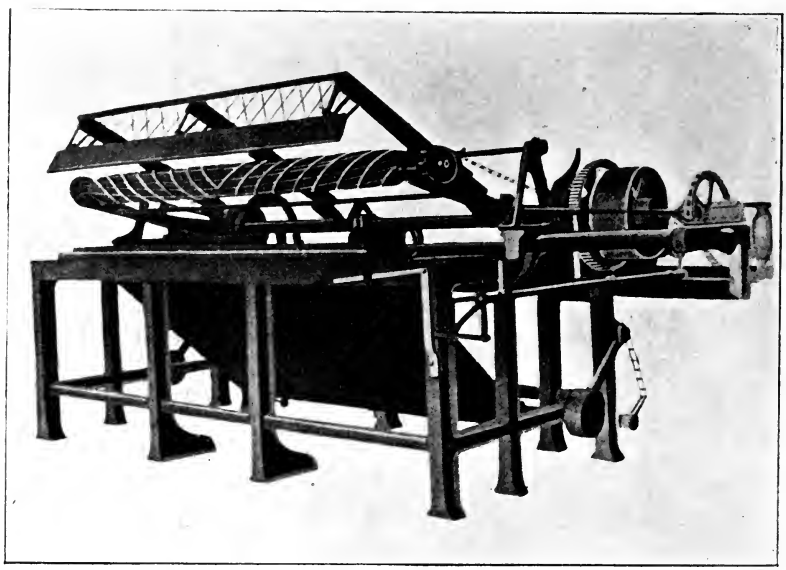


FIG. 24.—The Leidgen unhairing machine.

The other half of the hide or skin is then treated similarly. This machine, with a suitable cylinder, also works satisfactorily for fleshing, scudding, striking, scouring, etc., and many modifications of it are now on the market for these purposes.

The *Conus* unhairing machine (Fig. 23) (Moenus Machine Works, Ltd., Frankfort), is a machine of different type, the hide being thrown over a moveable cone which by rotation about its axis brings automatically the whole of the hide under the tools. These are fixed on an endless band, and work from

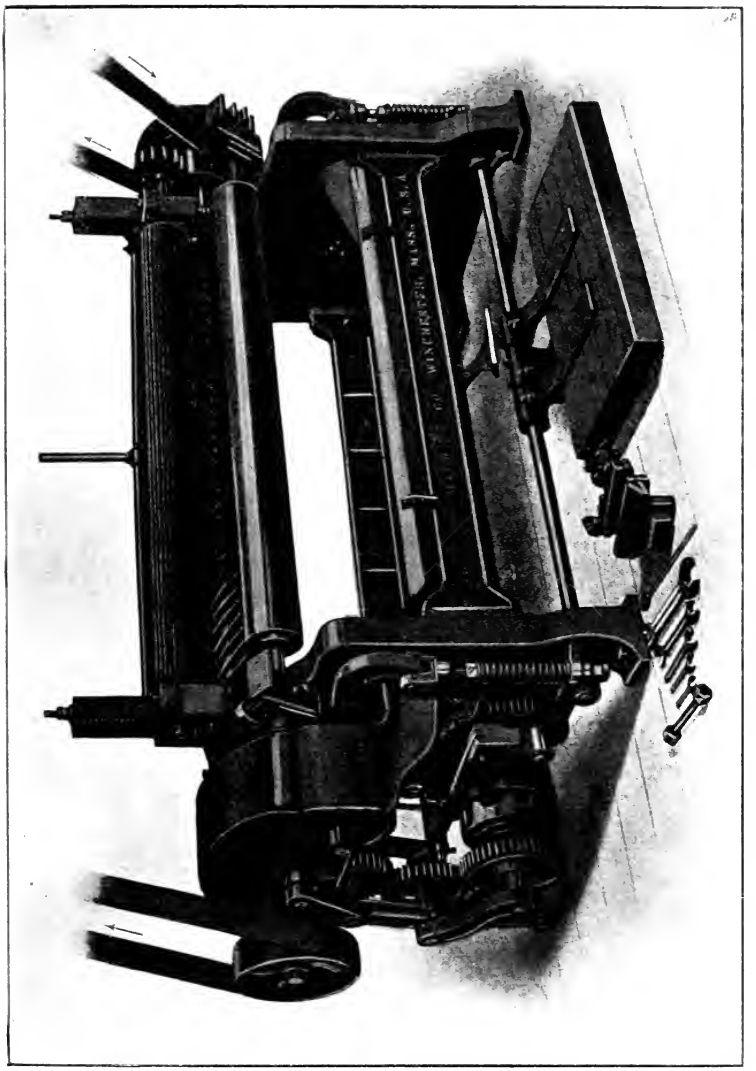


FIG. 25.—Whitney unhairing and fleshing machine.

the point of the cone outwards. No fixing arrangement is required, and the cone can be raised or lowered at will by the workman, thereby adjusting the pressure to the condition of the goods in various parts.

The *Leidgen* unhairing machine (Fig. 24) (The Turner Co.), more closely resembles the Vaughn in that the tool is a spiral knife blade cylinder. In this case, however, it is pushed down the hide which rests on a thick rubber apron stretched and arranged on springs. The pressure here also can be adjusted

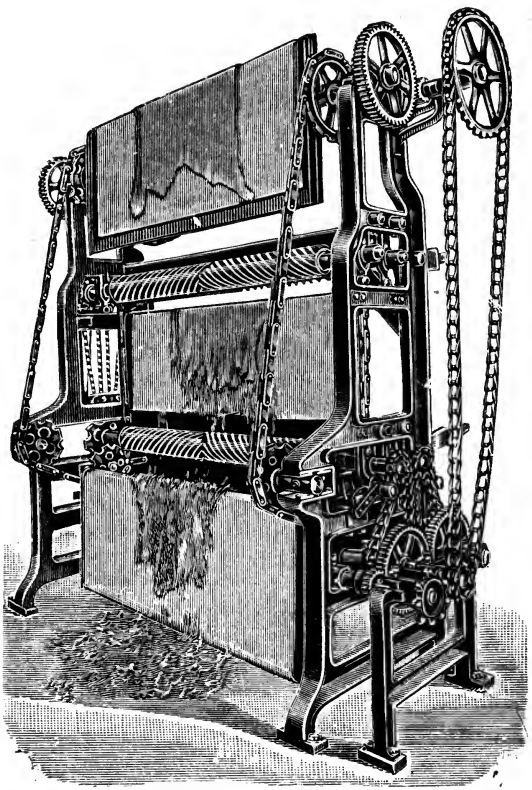


FIG. 26.—Serial Table unhairing machine.

to some extent by the operator, and it unhairs so that there is no need for further hand work.

The *Whitney* unhairing machine (Fig. 25), represents another type of machine. In this also a spiral knife blade cylinder is the working tool, but unlike the Leidgen the roll is stationary except for its rotations, and the goods are fed to it by means of rollers. It is used to a considerable extent

in the United States. The Turner *Serial Table* unhairing machine (Fig. 26) also represents a distinct type of beam-house machine, designed particularly for unhairing calf, goat, and sheep skins. The machine is fitted with three, four, or five tables, which continuously rise and fall. During their circuit they pass two separate pairs of cylinders, which remove the hair. Between the lower and upper cylinders the table covering is automatically shifted, thus allowing the upper cylinders to work that part of the skin which was not touched

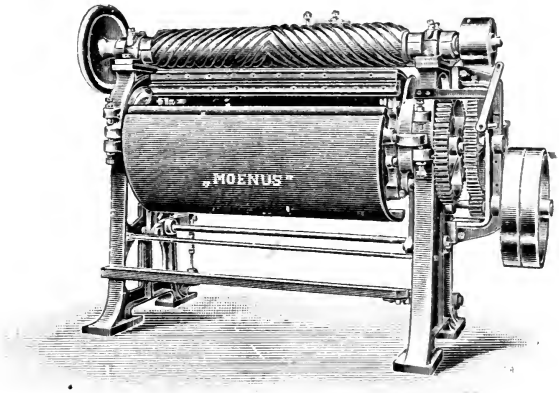


FIG. 27.—The "Continua" fleshing, unhairing, and setting out machine.

by the lower rolls. This machine is quite similar to the serial table setting machines (p. 335).

Drums and stocks have also been used for unhairing, but are not to be recommended. The former, however, are quite satisfactory for hides painted with sodium sulphide.

Fleshing machines are in much more general use and produce better results than unhairing machines, especially for the lighter leathers. The greatest danger is the tearing of the flesh. Some unhairing machines will also work as fleshing machines if the working tool be suitably changed. The Turner drum machine and the Whitney machine are both effective fleshing machines, but the former is not very suitable for heavy hides. The Moenus "*Continua*" (Fig. 27) is a semi-cylindrical drum machine, which is very suitable for

fleshing sheep, goat, and calf; and the "*Cylindra*" machine (Fig. 28), recently introduced by the same firm, seems also to possess some advantages. The *Wilson* fleshing machine (Fig. 29) is one of the very few machines suitable for fleshing hides for sole leather; it produces a clean cut with no tearing and little pressure, but has the disadvantage that it will only flesh the butts, so that the operation has to be completed by hand labour. The Turner *Rubber Roll* fleshing machine somewhat resembles the Whitney machine. A rubber roll carries the hide against the working cylinder and the grip rolls pull it out. Fig. 30 represents this machine as especially

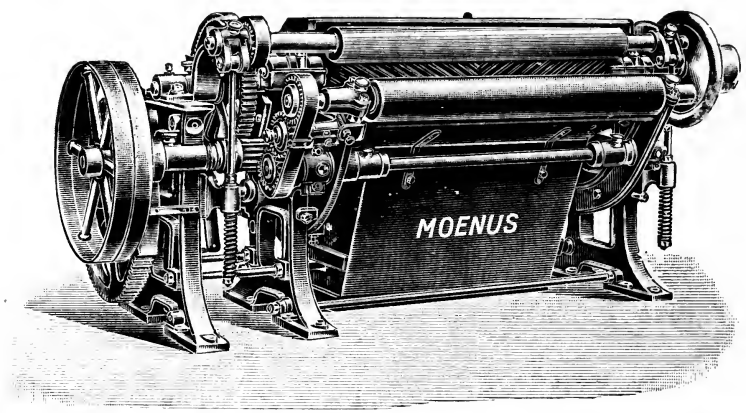


FIG. 28.—The "Cylindra" fleshing, slating, and setting out machine

adapted for skins. It takes considerably less power to run than the drum machines.

Many of these machines, by the use of modified working tools, may be used satisfactorily for "scudding" (p. 93), striking out, setting, scouring, etc. (pp. 259, 282). In the United States it is often usual to flesh hides out of the soak liquors.

There are many systems of working the goods through the lime liquors varying according to the class of leather which is being made. For reasons already noted it is quite general to place the goods in the more mellow liquors first and to arrange several neighbouring pits to work together and form a "round." In this way it is possible to arrange a continuous working, the

"tail" liquor being discarded where necessary and the new "head" liquor being freshly made up in the now vacant pit. In this way the lime liquors can be worked much like the liquors in the tan-yard (see p. 173). A deservedly popular

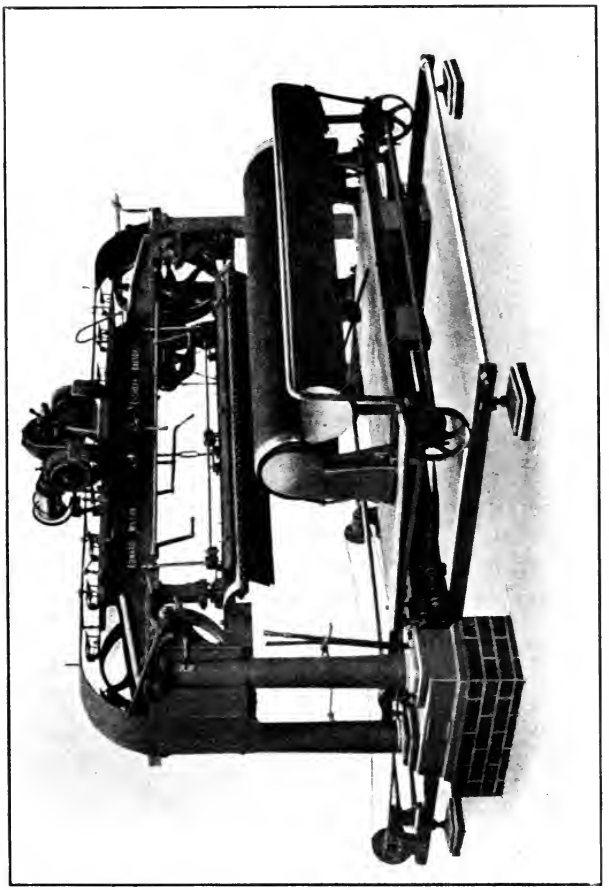


Fig. 29.—Wilson fleshing machine.

method for liming hides for sole and heavy leather is the **Three-Pit System** which is worked on the principle just described. The goods go into three liquors, first into an "old" lime, then into a "medium" lime, and lastly into a "new" lime. After once using the "new" lime becomes a "medium" liquor, and

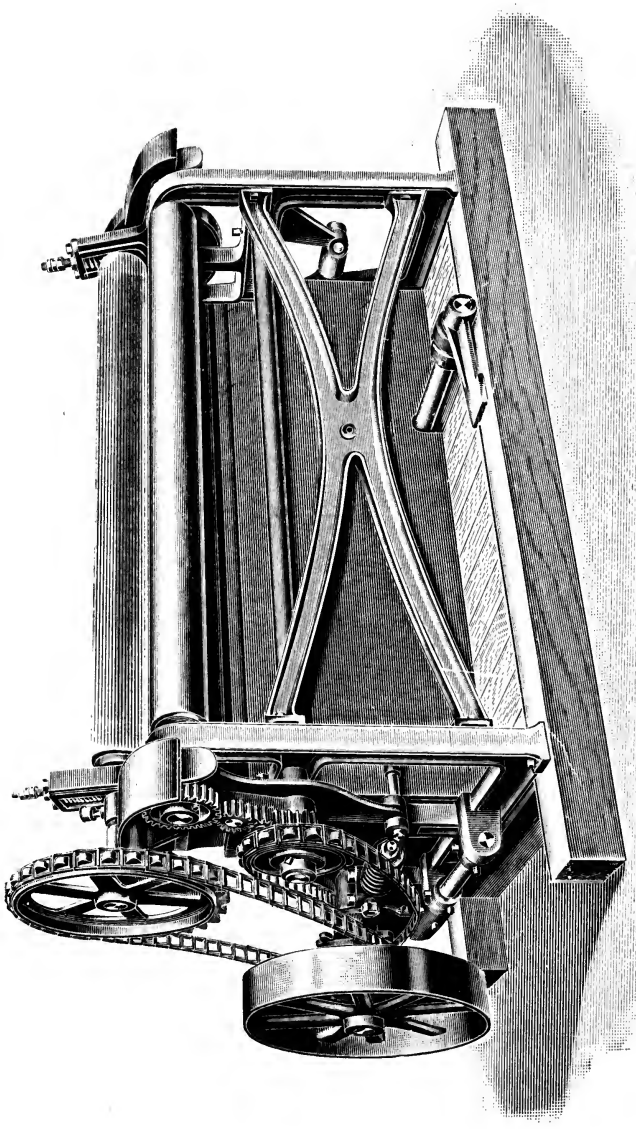
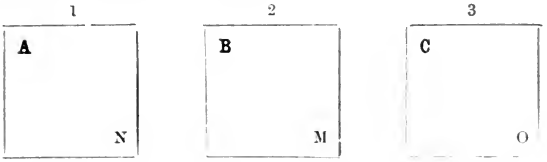


FIG. 30.—Rubber roll fleshing machine.

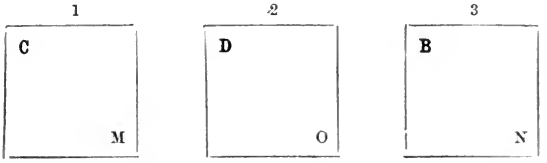
after again being used is then the "old" liquor which receives the green pack. After being used three times the liquor is rejected and the new lime is made up in its place. The goods

may be a few days in each liquor and are hauled as often as desirable. One great advantage of this system is that the top hides in one pit may become in the transfer the bottom hides in the next pit so that a regular treatment is assured.

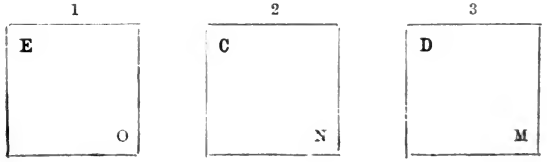
To make the system perfectly clear an example will now be given to show how the goods move through the liquors and how a "shift" may be brought about.



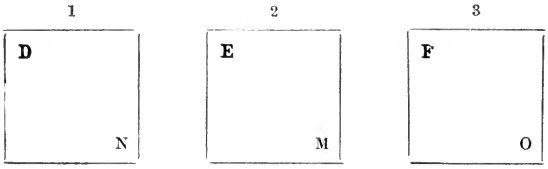
Pit 3 contains an old lime liquor (O) and the "green" pack (C), which has been in three days; pit 2 contains a medium lime (M) and the middle pack (B), which has been in this pit three days and in limes six days; pit 1 contains a new lime (N), and the pack next to be unhaired (A), which has been in limes nine days. The procedure is then as follows: pack C in pit 3 is hauled up on to the slope; pack A in pit 1 goes to unhair; the lime liquor in pit 3 is run away and a new lime made up in the same pit; the middle pack (B) in pit 2 goes now into the new lime in pit 3; the green pack (C) on the slope of pit 3 now goes into pit 1, which contains now the medium lime; the new green pack (D) goes into pit 2, which contains now the old lime. The position is therefore thus:



In three days the next shift is similarly brought about, and a new pack (E) brought into work. This results in the following position:



The goods remain in this position for another three days, hauling and setting occasionally, and precisely the same process is gone through, pack C going to unhair and a new pack (F) being placed in pit 3. This gives the original position again :



In this way each pack receives a nine days' liming, involving three days in each liquor. In winter, or whenever desired, one can give a shift after four days instead of three, and thereby obtain a ten, eleven, or twelve days' liming.

Another common mode of procedure is the **One-Pit System** or "**Bettering Method.**" In this case the goods enter a used lime liquor, and after hauling and setting for a few days the liquor is strengthened or "bettered" by the addition of more fresh lime. The goods again enter the well-plunged liquor and are hauled and set till ready for unhairing. It is often usual to place the hides at first in the unplunged liquor and after the first hauling to plunge up well. The liquor also may be bettered more than once by the addition of more lime. There are several disadvantages to this method of liming, not the least of which is the rapid accumulation of lime and inorganic matter in the pits, necessitating a thorough clean out at regular intervals. It will be seen, moreover, that at the end of the process the goods come out of a liquor which is by no means new and fresh, which indeed is so mellow as to be used for the first liquor of the next pack. For sole leather goods this is clearly a disadvantage, but it should be borne in mind that in a regular system of working a new lime will have to be made up for every two or three packs. This, of course, being done when the liquor is due to be bettered, and hence half or one-third of the packs will finish up in a fresh lime. For dressing leather hides, moreover, it is often desirable that the goods should not finish up in an absolutely fresh lime, and in this case the newly made-up lime liquors

should be "mellowed" by innoculation with part of the old lime which is being run away. A few inches of liquor may be left in the pit or a few bucketfuls of old lime liquor added.

The exact mode of procedure may be, perhaps, best explained by examples as before. In one process we have hides receiving a nine days' liming, and a regular cleaning out of the pits once in three weeks after two packs of goods have gone through. This system is carried out as follows:—

BETTERING METHOD (1).

Pack I.	*Pack II.*
Mon.—put into unplunged liquor.	Wed.—put into unplunged liquor.
Tues.—hauled, plunged, and set.	Thurs.—hauled, plunged, and set.
Wed.—hauled, plunged, and set.	Fri.—hauled, plunged, and set.
Thurs.—hauled, BETTERED, and set. (1-2 cwt. lime).	Sat.—hauled, NEW LIME made, and set.
Fri.—hauled, plunged, and set.	Sun.—let lie.
Sat.—let lie.	Mon.—hauled, plunged, and set.
Sun.—let lie.	Tues.—let lie.
Mon.—hauled, plunged, and set.	Wed.—hauled, plunged, and set.
Tues.—let lie.	Thurs.—let lie.
Wed.—hauled and unhaired.	Fri.—hauled and unhaired.

Of course there will be slight variations from this scheme, according to the time of year, and the class of hides, etc. In another one-pit process only a seven days' liming is given, but the limes are either somewhat mellower or contain some sulphide. The process may be carried out in the following manner:—

BETTERING METHOD (2).

Mon.—goods enter old unplunged liquor.
Tues.—hauled, plunged, and set.
Wed.—hauled, BETTERED with ½ cwt. lime, and set.
Thurs.—hauled, plunged, and set.
Fri.—hauled, BETTERED with 1½ cwt. lime, and set.
Sat.—hauled, plunged, and set.
Sun.—let lie.
Mon.—hauled and unhaired.

The **Pullman-Payne process** already mentioned aims at quickening the operation of liming. The goods are placed first in a 1 per cent. solution of caustic soda for two days, and after some draining are passed into another pit containing a 1½ per cent. solution of calcium chloride, in which they

remain also for two days, and then go into water. This process will not loosen the hair unless the goods have been previously steeped in a putrid soak for about 36 hours, and this undesirable and dangerous procedure constitutes the great disadvantage of the method. It is, however, useful for obtaining the true liming effect on skins which are not to be unhaired.

The **suspension systems** involve the use of agitators in the lime pits which keep the milk of lime thoroughly mixed and save frequent hauling. Many patents have been taken out for such methods. In one variety the liquor is circulated between the suspended hides by means of pumps, which raise up the liquor and sludge from the bottom. In another method the circulation is caused by a screw propeller which is worked below a false bottom in the pit.

Practical Methods of Liming.—The following account will illustrate the nature and extent of the liming which is given to the different classes of goods; but it will be understood that there is nothing cast iron about the figures given, partly because no two yards make the same goods, and partly because the duration of the liming is, of course, judged by the fitness of the goods for unhairing, and this varies considerably with the time of year, being distinctly shorter in the summer months.

Hides for sole leather receive a short, "sharp" liming, but there are wide variations in treatment according to the class of hides used and the quality of leather being produced.

For ordinary fresh market hides which are to made into "scoured bends" after a mixed tannage, the three-pit system of liming is now very general. They should receive about three days in each liquor, hauling every day in the first liquor and once in each of the others, the goods remaining piled for an hour or two to assist in removing creases. About 10 lbs. of lime for each 70 lb. hide is taken when making up a new liquor. If caustic soda be used to assist in plumping, about 2 ozs. per hide may be employed, and in this case 8 lbs. of lime per hide will be sufficient. In the short hair season it will be advisable to use a little sulphide to assist in complete depilation, and in this case about 9 lbs. of lime per hide is used to

make up the new lime, and 2 ozs. of sodium sulphide per hide may be added to the medium lime, *i.e.*, after the liquor has been used once. Each pack therefore passes through two sulphide limes and one fresh ordinary lime. The goods are best unhaired by hand labour, but the Wilson machine may be used to assist in fleshing.

For high class oak-bark tanned sole leather, good Continental hides (Italian, Hungarian or Bavarian) are employed, or the best Scotch Shorthorns, and after appropriate soaking are limed by the three-pit system like market hides. The one-pit system, however, is also in use.

For the West of England tannage of "bloomed butts," heavy South American salted hides are employed and are given a distinctly longer and stronger liming. The three-pit system may be used, but rounds of more than three pits are also convenient. The new liquor is made up by using 12 to 16 lbs. of lime per hide, and the liquors are plunged well when the goods are hauled. The hides remain in the liquors 14 to 18 days and in winter even up to 21 days. The liquors are sharp so that there is not much solution of hide substance, but it would probably be better to give a longer soaking and to use a little sulphide in both soaks and limes to reduce the time of liming. In rounding it is usual to cut long butts and narrow bellies.

For the quick drum tannage in extract liquors (pp. 178, 192) it is essential for the rapid penetration required that the hide fibres should be thoroughly split up into the finer fibrils of which they are composed, and hence a somewhat long and sharp liming is given of about 14 days. If the limes are kept sharp there will be little danger of any undue loss of hide substance.

In the United States and on the Continent a common way of depilating sole hides is the so-called "Buffalo" method of liming. This involves the use of warm water, which largely increases the chemical and bacterial action, so that a quick process is obtained. The method can also be modified by the use of the sulphydrates. One mode of procedure is to give one day in an old lime, one day in a medium lime, one day in a new lime, and to throw the goods into warm water at 40° C

They will then be ready to unhair in 6 to 8 hours. A large American firm used the following process on packer hides. After 4 days' soaking the goods were limed with 2 lbs. of lime and $2\frac{1}{2}$ ozs. of sodium sulphide per "side" for 10 hours. They were then thrown into water at 35—43° C. and left overnight. Next morning they unhair easily. A Continental firm give a 2 to 3 days' liming in liquors to which a little "tank waste" has been added. The hides are then thrown into water at 32° C. for 6 to 8 hours, unhaired, returned to warm water, and then scudded. These examples are perhaps sufficient to illustrate the idea of the method. It will be seen that the chief advantages are the rapidity of the process, which not only is an advantage in itself but causes also a smaller loss of hide substance, and the washing of the hide free from lime. On the other hand, however, the "grease is not killed," *i.e.*, the fatty matters of the hides are imperfectly saponified during the short action of the lime, and the fibres are not sufficiently swollen and plumped, necessitating in some cases the subsequent "raising" of the pelt with vitriol.

Short liming processes are also employed which depend upon the use of larger quantities of sodium sulphide to assist the lime than those suggested above. From 2 to 12 ozs. per hide may be employed with success in addition to 7 to 8 lbs. of lime per hide, but the larger quantities are liable to give harsh grain and act deleteriously upon the hair.

Another type of quick unhairing methods is that in which sodium sulphide is used in strong solution and with possibly some lime as an assistant. In one process a 30 to 40 per cent. solution, thickened with lime, is painted on the hair side, using $2\frac{1}{4}$ lbs. of sulphide and about 1 lb. of lime per hide. This is well brushed into the roots of the hair with a cane brush and the hides are folded up and packed into a tub or pit. The rest of the "paint" is mixed up with water and poured into the pit, which is then filled up with water. The hair is reduced to a pulpy mass and can be brushed off in a few hours, the exact time varying with the strength of the solution. Another process used with some success is to employ a shallow tank, wide enough to take a hide flat, containing a 30 to 40 per cent. solution of sodium sulphide and

possibly a little lime. The hides are drawn into this liquor by means of hooks or strings and brushed well whilst still in the solution. They are then drawn out to pile on a sloping floor, from which the liquor drains back to the tank. The hides unhair in a few hours as before. Yet another process is to suspend the hides for a few hours in a solution of sulphide of about the same strength and then to unhair as usual. To each of these processes, however, there are a number of disadvantages. The hair roots are apt to be left in, causing an unsightly appearance on the finished goods; the hair, which has some commercial value, is total loss; the grain is liable to be injured, being rendered temporarily tender by the sulphide; the goods often receive stains from the impurities in the commercial sulphide; the caustic action of the liquors on the hands and nails of the workmen makes it a nasty process for them; the short time admits of very little plumping and grease saponification, which causes "bad weights" and "greasy bends" respectively. It will be understood, therefore, that these processes are only suitable for the cheaper classes of goods, and are not very widely practised.

Hides for belting leather usually receive much the same liming as sole hides, but often somewhat longer and mellower. Especially where no bating is given, as is now usual, an extra day or two in limes may be helpful in producing the requisite pliability. The quick processes with strong solutions of sulphide have also been employed successfully.

Hides for harness leather receive a distinctly longer liming than sole leather goods, but the exact time depends upon the class of harness being produced; from 10 to 16 days, however, represents the range of variation. The liming process is also dependent upon the deliming process. For the cheaper classes of harness goods it is now usual to replace bating by a mere chemical deliming, and where such treatment is given a somewhat long liming should be given also in order to obtain a sufficient solution of hide substance to produce the flexibility required. Either the three-pit system or a bigger round of liquors can be used, with a little sulphide in the short hair season. Harness hides are rounded into "backs" or long butts.

Dressing hides (for upper leather, etc.) receive a 14 to 16 days' liming in mellow liquors. The one-pit system is commonly employed, but a round can also be used with advantage, and of course the three-pit system can be quite well used, remembering to add always a certain amount of old lime liquor to the fresh lime as it is made up. For the cheaper classes of goods sulphide may be used and a shorter liming given (7 to 10 days). This is desirable for chrome work ("box sides"). Dressing hides are often not rounded till after tannage, though occasionally cut into sides, and hides for bag work are not rounded at all.

E. I. kips receive very similar treatment in the limes, remaining 14 to 16 days in mellow liquors, hauling every day. A round of seven liquors is commonly employed, moving the goods forward every second day. No sulphide is added as a rule, but a little comes in from the soaks. Red arsenic is sometimes used.

Calf skins receive rather different treatment according to their destiny. For boot and shoe work (vegetable tannage) a mellow sulphide liming of 10 to 14 days is given, using 2 cwt. of lime per pack of 200 to 250 skins. In the tail liquors of the round the goods are hauled every day, and 1 per cent. on the lime of sodium sulphide (*i.e.*, $2\frac{1}{4}$ lbs. per pack) is used in these liquors. In the head liquors the goods are hauled and handled forward on alternate days, but no sulphide is employed. A mellow liming of 3 weeks can also be given without the use of any sulphide.

For box calf and willow calf, etc. (chrome tannage), a very short liming is essential, 4 to 7 days being ample, and, of course, in this case a considerable amount of sulphide is employed. The minimum solution of hide substance is desired for this tannage, but not so much sulphide should be used as to cause harsh grain.

For calf kid (alum tannage) the goods receive a not very mellow liming of about three weeks. No sulphide should be used unless it be red arsenic, and the goods should never enter a quite fresh lime liquor.

For bookbinding and fancy purposes (sumach tannage), the skins receive a mellow liming of 18 to 21 days.

A round such as just described for shoe calf is successfully employed, slaking the 2 cwt. of lime with 20 to 30 gallons of old lime liquor, and using no sulphide.

Sheep skins and lamb skins are fellmongered by methods which differ widely with the class of goods to be unwoolled.

The sweating process (or "staling" process, as it is often termed with these goods) is used to a considerable extent both on the Continent and in this country for unwoolling these skins, for although it is very liable to injure the pelt and give weak grain, it gives, on the other hand, a very satisfactory yield of wool in good condition. It is therefore employed where the wool is important, and also for dried and salted foreign skins. The fresh skins enter the "first soaks" until the next day, clean water being, of course, used. If the skins are salted or dried they are returned to a fresh water until sufficiently softened. The skins go direct from the soaks to the "burring machine," which consists essentially of a set of spiral blades rapidly revolving against the wool of the skin. The skin is drawn up and down on an inclined table by means of reversing geared rollers, and a good supply of clean water is constantly flowing over the skins during the process. All dirt is removed from the wool in this way. The goods now enter the "second soaks," remaining 24 hours or more in clean water. They are then drawn and laid flat to drain. The "tainting" or "sweating" stoves are now entered. These are air-tight chambers of the type mentioned (p. 57). They are fitted up in this case with wooden rails and hooks attached. The well-drained skins are hung on the hooks by the fore shanks, flesh to flesh, and the tainting is given a "start" often by the injection of live steam. The skins are ready for pulling in times which vary from 6 to 8 days in summer and 12 to 14 days in winter. No rules can be given for the control of the process; the smell of ammonia in the stove, the condition of the goods, and the experience of any man with any one stove, are the best criteria. Long-woolled skins are sometimes "slimed" about halfway through the sweating process, *i.e.*, they are worked over the beam on the flesh to remove fat and grease. When in proper condition the wool is pulled and the pelts are paddled in water or a weak

mellow lime. The skins now enter the lime liquors and are "limed up" from mellow to fresh liquors. This subsequent liming is necessary to kill the grease in the skins, for this grease is not saponified or removed in sweating. The skins are next unhaired, returned to fresh lime, and sold as soon as possible to the leather manufacturer.

Another method used with success in this country involves the use of lime before sweating. The skins are first thrown into a soak pit of clean water. Clean water should be constantly running into this pit, and beneath a false bottom is an outlet with an eased plug to allow a constant escape of the soak liquor. After 24 hours or more the skins are taken out and carefully "broken over" the beam or put under the burring machine. They are then spread out, flesh side up, and painted over with a creamy mixture of lime and water by means of a mop. The mixture should be well up to but not past the edges. The skins are now placed in a pit, and sometimes "flooded" by filling up the pit with water. Difference of opinion exists as to whether it is better to flood at this stage or not, but it is probably better as a rule to do so, for although the wool is not so good the pelts are distinctly better and all heating or "specking" is prevented. The skins remain thus for about two days and are distinctly plumped. They are then drawn through fresh water to wash off the loose lime, laid in pile flesh to flesh, and again rinsed more thoroughly. They are now horsed up to "sipe" or drain, till ready for the sweat pit or tainting house. In this the proper "pitch" is got up by means of the steam pipes on the floor and the process is carried on as usual. The skins are then taken to the pulling shop. The "long wools" or "wool skins" are placed over the "pulling beam" with two or three pelts, flesh up, to act as bolster, and the true wool is pulled by hand, keeping separate wool of differing quality, according to the breed, age and sex of the animal and the part of the body from which the wool is taken. Thus are obtained ewe wool, wether wool, hog wool, lamb wool, etc. The "rubbing knife" is next carefully applied to the hairy parts on the shanks and faces, this hair being kept carefully separate from the wool. The pelts are then placed into water,

then into a weak fresh lime for one day, and then into a strong fresh lime in which they are handled frequently until sold to the leather manufacturer. In unwoolling "Downs" and "short wools" the skins are bolstered as usual, and the rubbing knife applied first to the shanks, hairy parts and the coloured parts. The hair and wool thereby obtained are carefully cleared away and the whole skin now rubbed and pulled, keeping separate wools of different length. The unwoolling of "mountain breeds" is somewhat intricate because of the intermingled hair and differing quality of wool. In this case therefore the procedure is to remove first the best quality of wool, then the inferior qualities, and then to throw the skins into limes. They are limed four days in weak limes, paddling three hours each day, and four days in strong limes, paddling similarly. They are then unhaired and fleshed. In unwoolling shearlings or "pelts" the rubbing knife should be applied with great care so as not to damage the grain, and in this case also the true wool is kept separate from the hair and from the other wool. Shearlings are also sometimes limed in ordinary lime liquors for 9 to 14 days, hauling frequently. They are then unwoolled without sweating.

Another type of fellmongering much used in America and now common in this country involves the use of sodium sulphide as a depilatory, a solution of this being made into a creamy mixture with lime and painted on the flesh side of the skins, which are folded up or piled flesh to flesh until ready for pulling. The skins, after efficiently soaking and cleansing, are drained over horses or put through the "wringer" to eliminate water. They are then painted on the flesh with a mop with the sulphide mixture, taking great care to keep the solution from coming in contact with the wool, and putting more of the paint on the neck and along the back as these places unwool less readily. The strength of the sodium sulphide solution determines the rapidity of the depilation. The solution may range in strength between 14° and 24° Beaumé according to the class of skins, thin skins requiring the weak solutions, and thick skins or salted skins the strong solutions. The lime should be thoroughly slaked to a stiff paste and several pailfuls of this added to a barrel

full of the sulphide solution. The wool will be loose in a few hours, but it is thought better by some to leave the skins folded up until next day before pulling. It is desirable that the skins should not be allowed to heat in summer or to freeze in winter, and consequently the exact treatment differs somewhat with the strength of depilatory and with the season. Some firms use a 25 per cent. solution of sodium sulphide; this is made creamy with lime, painted on the flesh, and the skins placed in pairs flesh to flesh. When about three dozen skins have been painted the first pair are ready for pulling. Another way is to use sulphide only in strong solution, the goods are piled flesh to flesh for one hour and then pulled. All these methods of depilation depend purely on the chemical action of the sodium sulphide on the hair root, and the method of painting on the flesh side is efficient for sheep skins because the wool root is very deeply seated in the corium, being one-third to one-half the way through the pelt. The porous and spongy texture of the corium also assists in making this method of operation possible. After pulling the wool the skins are opened out and dropped into clean water and washed. The unhairing is now completed by liming in pits in the ordinary way, from mellow liquor to fresh, hauling frequently. They may be limed thus for 4 to 6 days. This plumps the pelt, separates the fibres and kills the grease. This liming is as necessary as if the skins were sweated, for the grease is very little affected by the sulphide depilatory, and sheep skins contain a very large amount of grease (5 to 15 per cent.) compared with ox hides (2 to 3 per cent.) and other skins. After liming and unhairing, the fellmongering is complete.

Kid skins and lamb skins for "glove kid" are treated usually in rather special ways which are of great importance in producing the qualities desired in this class of leather. A certain amount of interfibrillar substance should be dissolved in order to obtain the property of "stretch," *i.e.*, of extending in any direction without springing back. At the same time it is desirable to avoid old lines which tend to make a loose, porous leather with a dull grain. Liquor containing sodium sulphide should also be avoided on account of its harsh effect

on the grain. It is furthermore necessary that the fat should be fully saponified and removed or difficulties occur in dyeing the goods. Hence it is common to employ arsenic limes for these goods, using about 1 per cent. of arsenic on the weight of the lime when making up the liquors. The goods should remain in these liquors 7 to 10 days. Some firms use rather more arsenic: 5 per cent. of lime and 0·1 to 0·3 per cent. of red arsenic on the green weight of the skins. The liming then lasts only 4 to 5 days. Good results have also been obtained by liming for about 14 days without arsenic but with new limes. Another short method (Eitner) is to use 15 litres of lime paste for 500 skins, and place the skins in this liquor for one day. On the next day and also on the third day another five litres of lime paste are added, and on the fourth day five litres of paste which contain 10 per cent. of arsenic. Next day the skins are unwoolled and washed. It is now common, however, to unwool lamb skins by painting the flesh with mixtures of sodium and lime as described above. It is desirable that skins treated thus should be pulled as soon as possible and placed in cold water. Gas lime and other depilation paints have also been employed successfully. Whatever process has been employed the pelts after unhairing are thrown into a very weak lime for a short time and then "levelled," which includes fleshing and the trimming of the head, ears, shanks and flanks. They are then thrown into soft water or weak lime till ready for puering.

Goat skins, for moroccos, glacé kid, etc., receive 16 to 21 days' liming in summer and about 3½ weeks' in winter. They are slightly more difficult to unhair than some other skins and require a fair amount of hide substance to be dissolved in order to produce the desired softness in the finished leather. They are given two rounds of liquors. The first series consists of mellow arsenic liquors, 6 per cent. of red arsenic being used on the weight of the lime. The goods should be hauled frequently, and remain in these liquors about ten days. The skins are then unhaired, flushed and placed in a second series of limes to plump. These are new limes containing up to 6 per cent. of caustic soda on the weight of the lime. The goods go through this round in about 10 days. Sodium

sulphide limes may be used in the first round instead of arsenic limes, and the skins may then be unhaired in 4 to 5 days.

Seal skins, after soaking and blubbering, are fleshed before entering the limes. They receive a long liming in mellow liquors without any sulphides. This is necessary to kill the grease. About three weeks in limes is usually sufficient. A one-pit system is most convenient, but some firms finish up in new limes. The older animals are very liable to show "ribs" in the pelts which are difficult to remove. When the skins are sweated, however, this trouble does not occur.

The Chemical Control of the Lime-yard.—The "**available lime**" in a sample may be determined by a 0·1 per cent. solution with hot distilled water, cooling, making up to mark, and titrating an aliquot portion of the filtrate with N/10 hydrochloric acid. Each cc. used corresponds to 0·0028 per cent.

Sodium sulphide may be titrated with N/10 acid and methyl orange, as that indicator is unaffected by sulphuretted hydrogen. Any caustic soda will be included in this, so that to determine the amount of sulphide proper it is necessary to titrate the solution with N/10 zinc sulphate solution, using lead acetate as an outside indicator for the complete precipitation of the sulphide.

Ammonia in lime liquors may be estimated by distilling 100 cc. in the Kjeldahl apparatus (p. 398), and collecting the ammonia in standard acid, or more accurately by the method of Procter and McCandlish.[1]

Dissolved hide substance, which is not only important in itself, but is also the best criterion of the "mellowness," of the age and of the bacterial activity of a lime liquor, can be determined by the Kjeldahl method after acidifying and evaporating, or by the formaldehyde method suggested by the Author.[2] For mere control work, however, the best method is to estimate dissolved hide substance empirically by means of a simple titration with phenol phthalein and with methyl orange.[3]

[1] J.S.C.I., 1906, 254.
[2] Bennett, J.S.C.I., 1909, 291.
[3] Bennett, J.S.C.I., 1909, 292.

The lime liquor should be filtered through the Berkefeld filter candle (p. 146), or through S. and S. "605" paper, and 25 cc. titrated in a porcelain basin with N/10 hydrochloric acid and phenol phthalein. Methyl orange is now added and the titration continued to a distinct red. The difference between the two titrations represents the acid consumed in neutralising the weak alkalies (amines, calcium salts of weak acids, etc.). These are proportionate to the amount of dissolved hide substance. For ordinary lime liquors 1 cc. titration difference corresponds to 0·0053 grams of hide substance. In cases where a small amount of sodium sulphide is used to assist in depilation a constant error is introduced, and a different factor will have to be used according to the amount of sulphide. The titration also must in this case be conducted in dilute solution.

Caustic lime in a piece of hide may be determined by the direct titration of the finely sliced piece with N/10 acid and phenol phthalein, but the titration should be continued until a permanent discharge of the pink colour is obtained.[1]

The **hide substance** in a limed hide may be determined by weighing it when completely immersed in water. Weight in water × 3·38 = weight of hide substance.

[1] Cp. Bennett, J.S.C.I., 1907, 455.

CHAPTER VIII

DELIMING

It is intended in this chapter to give some account of those operations which are associated with the preparation of the limed hide or skin for the tanning liquors, for the necessity for some such preparation is clearly evident when it is observed how readily all vegetable tanning matters oxidise and darken in the presence of caustic alkalies. The neutralisation and removal of caustic lime is thus a matter of some importance and has therefore given the title to the chapter, but there are several other operations and changes associated with this process which for certain classes of leather are almost equally important and which are conveniently dealt with also at this stage.

For the softer and finer leathers it is usually necessary not only to effect a complete removal of the lime, but also to reduce the swelling and plumping that has occurred in the limes, and to allow some bacterial action on the interfibrillar substance in order to produce the requisite softness and pliability. These changes are usually accomplished by *puering* and *drenching*. Puering consists in treating the goods for some hours with a warm fermenting infusion of dog-dung, which assists in the removal of the lime by both chemical and mechanical action, and which allows the bacterial enzymes to bring into solution a certain amount of hide substance. Drenching, which consists in steeping the goods in a fermenting infusion made with bran and hot water, is usually a subsequent process, and assists in cleansing the skin, in completing the neutralisation of the caustic lime, and perhaps also in slightly plumping the pelt with the organic acids it contains.

For harness and belting leather, upper leather, etc., a much

more moderate treatment is desirable; but a certain amount of flexibility is required so that the goods are generally *bated*. This process is similar in principle to puering, but the dung of pigeons or hens is used to make the infusion, which is used cold over a period of several days. These goods may be drenched or further delimed by means of acids.

For sole and heavy leather, in which weight and firmness are primarily required, no softening or reducing of the pelt is desirable, and no bacterial action should be allowed. Hence it is usually quite sufficient to neutralise the surface lime by a bath of weak acid and to pass therein to the tan liquors, the natural acidity or "sourness" of which will complete the neutralisation and keep the material well plumped.

FIG. 31.—Scudding with a hand knife.

For all goods the delimed or partially delimed state is a convenient stage for further cleansing from fatty matters, lime soaps, small hairs, hair sheaths, pigment, dirt, etc., and this is accomplished by working over the beam again (Fig. 31) with a "scudding knife," which resembles the unhairing knife but is rather sharper (see Fig. 21). A hand knife is also often used. It is sometimes further desirable that some mechanical working and shaving of the pelts ("bate shaving") should take place to assist in softening the thicker parts and in rendering the goods of even texture.

Puering, which involves the use of a fermenting infusion of

dog-dung, has long been used in the manufacture of morocco and glove leathers. It has never been regarded as a satisfactory process, not only on account of the revolting nature of the material, but also because of its variable quality and the consequent uncertainty of the results obtained by it. The food of the dog, the accidental or even deliberate adulteration with water or sand, the age of the material and the manner

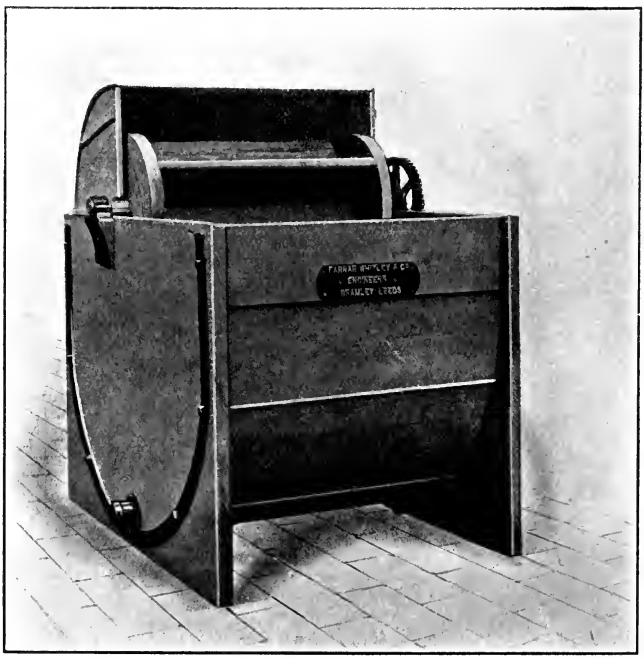


Fig. 32.—Puering paddle.

in which it has been kept, are all factors which extensively influence the puering process. The moisture content of different samples of dung has been observed to vary between 4 and 85 per cent., and some samples have been found to contain quite 50 per cent. of inorganic matter. An extensive analytical investigation, moreover, is not justified by the value of the results obtained, so that the only way is to endeavour to obtain as regular and fresh a supply as is possible. Dung

obtained from kennels, therefore, is far better than that from the streets, which latter is liable to contain a very indefinite proportion of dirt. Dry dung should be of a fairly light colour; dark or black dung has undergone an improper fermentation and is unsuitable for puering. Fresh dung is best kept in a dry condition and as little exposed to the air as possible. It has been discovered, however, that the puer bacteria are not present in the dung when excreted, so that it is necessary to mix it into a paste with water and allow it to ferment for some weeks before use, and it is often convenient to have a series of such pastes made up in casks from which they can be drawn when ready. It is stated that dung should never be kept over three months in this condition, and probably at least a fortnight is required for the growth of the true puer ferment, but both these times are no doubt dependent on the material, the season, and the manner of storing.

In making up the liquor it is usual to dilute the required amount of dung paste with warm water and strain the stirred infusion through coarse cloth into the paddle, and then make up with a further quantity warm water. The great variation in the quality of the material makes it quite impossible to specify any particular quantity to be used per weight of pelt, and it is therefore necessary to rely merely upon empirical observations of its rapidity of action in "pulling down" the skins; but in any yard the number of "pailfuls" per pack is soon found out and varied as necessary. The temperature of the puer liquor is a very important point, as some skins are very liable to be "scalded," and the time for which the goods should be treated is also dependent on this, being longer for lower temperatures but varying also with the thickness and nature of the skin. It is also difficult to state precisely the condition of skins after sufficient puering. They should, however, be thoroughly relaxed and flaccid, and the swelling pulled down so that they are in a very soft and "fallen" condition; the springiness and elasticity of the plumped pelt should also have completely disappeared and the impression of the thumb or hand should be readily retained. The grain should appear white and feel soft and silky, and the flesh side tender and easily torn with the finger nail. The thoroughness

with which this change is accomplished varies, however, for different skins, and judgment based on practical experience is the only reliable guide in this matter. The extent to which lime is being removed can be readily tested in this or any other deliming process by moistening a freshly-cut section of the skin with two or three drops of phenol phthalein solution—the familar pink colour appearing where caustic alkali still remains.

The nature of the process has been long understood as partly chemical and partly bacterial, but its precise mode of operation was quite obscure until cleared up by the researches of J. T. Wood. To find the cause of puering he investigated first of all the action of the digestive enzymes on the limed pelt, as there is little doubt that these occur in fresh dung. His results indicated that *pepsin*, if contained in the dung, has practically no influence in the process, and that *trypsin* only contributes to the action in a very minor degree, partly in pulling down the pelt and partly in emulsifying the fatty matters of the skin. He then examined the action of a fresh puer liquor freed from both organised and unorganised ferments by boiling, and found that although there was considerable puering action it was confined merely to the removal of lime, and that no loss of interfibrillar substance occurred under these conditions owing to the absence of all fermentive action. The deliming action was discovered to be principally due to the salts of the amines with organic acids, the caustic alkali displacing the weak organic bases. The hydrochlorides of organic amido compounds were found on experiment to give a similar result. Wood next investigated the bacterial side of the puering process and attempted to determine the species which would yield pelts of the requisite texture. None, however, that were isolated gave such a powerful puering effect as an ordinary puer liquor, and hence he concluded that the process demanded both the chemical and bacterial actions for satisfactory operation. He further discovered that the puer bacteria did not act directly on the pelt but that the action was really due to the enzymes they discharge; and these enzymes with the assistance of mixed amine hydrochlorides, and in the absence of any organised

ferments, were found to pull down limed pelt like an ordinary puer liquor. Puering, therefore, is due to the enzymes of the bacteria which collect on fermenting and exposed dog-dung and which thrive under the ordinary conditions of the process; and these cause some of the gelatinous matter of the skin to be brought into solution. It is also due to the amido salts which occur in dung and its decomposition products and which act merely as deliming agents; and in a much smaller degree to the enzymes already present in fresh dung. In view of the uncertainty associated with ordinary dung and the disgusting nature of the material, it was very natural that Wood should proceed to make up an artificial puer by means of a suitable culture medium, which could be inoculated with prepared cultures of suitable bacteria before use. This he has been able to do with considerable success, so that both bacterial culture and culture medium are now on the market under the name of *Erodin*.[1] In its use 1 per cent. of the solid medium on the weight of pelt is dissolved to form a 2 per cent. solution, which is heated in a cask by steam to a temperature of 40° C. The culture of *Bacillus erodiens* is then added and the solution kept above 25° C. for 3 days, warming up to 40° C. each morning. About half of this liquor is taken and the fermentation continued by the addition of more of the sterile 2 per cent. medium solution; more *Bacillus erodiens* being also added occasionally. This process is now widely used both in this country and on the Continent, giving results of much greater certainty and safety, and yielding puered skins quite free from the objectionable stains which are often experienced with the less definite dung puer.

Bating, which in principle is the same as puering, is usually carried out in the cold and applied to heavier goods which are to be made into pliable leather. It involves the use of the dung of hens and pigeons instead of that of dogs. In this case also it is usual to make up the infusion in a separate vessel by adding warm water and allowing the mixture to stand for a day or two. When the fermentation is thus started, the infusion is filtered from insoluble organic matter

[1] Drs. Popp and Becker also worked independently on these lines.

by passing through sacking into the pit prepared for the goods; this prevents "bate-burning." The goods should now go in for several days, hauling frequently to ensure even action. It is found in practice that the bate liquor must be neither very alkaline nor very acid for satisfactory results. A bate liquor can be "mended" by the addition of a further quantity of dung infusion and by the precipitation of lime, as oxalate by the addition of oxalic acid, but this must not be carried too far, for the organic matter in solution and the bacterial activity would then rapidly increase and become dangerous. The nature of these bacteria has not yet been thoroughly investigated, but they are no doubt different from the *Bacillus erodiens*, which thrive in a warm puer, and seem to consist chiefly of *micrococci*. It is not uncommon, however, especially in the United States, to use warm bates. In this case it is a question whether the prominent bacteria are the same as for cold bating. In carrying out this process the hides are placed in a tumbler or large paddle and the bate kept at about 35° C., which brings about the desired effect in a few hours.

It is obvious that an effect is obtained very similar to bating by a longer liming in mellower liquors, and cases have been already noted in which either alternative may be chosen with satisfactory results. Where the bate is not used in these cases, some deliming acid must be substituted. The action of the bate is generally understood to be less drastic than the puer, both in its bacterial and purely chemical effects; the process being slower, a more even result is obtained and the leathers resulting are not so loose and soft. Many artificial "bates" have been put on the market, but they are mostly deliming agents only and often even antiseptic! Some fermentive mixtures have, however, been suggested. An American "bate" involves the use of glue, glucose and blue cheese, and is perhaps good enough for belting offal, etc., but its action is more like that of the drench.

Drenching, as a rule, follows puering or bating, but in some cases it is used as a substitute for these. In this process an infusion of bran is made by scalding it with hot water and allowing it to stand until it reaches a temperature of about

35—40° C. A few buckets of an old drench liquor are then added to inoculate the infusion, and after mixing, the drench pit is brought to the required temperature by the addition of cold water. The goods are then inserted for the required period, which varies largely with the temperature and class of skin or hide The *modus operandi* of the drench has also been made clear by the investigations of Wood. The enzyme *cerealin* which occurs in the bran converts the bran starch into glucose, which then can form the food of the drench bacteria, *Bacterium furfuris* α and β. By the action of these organisms, appreciable quantities of lactic, acetic and other acids are formed, together with some evolution of hydrogen, carbon dioxide, nitrogen, methane and sulphuretted hydrogen. The organic acids act as neutralising agents for any remaining caustic lime and may even plump the pelts slightly and so fit them for tanning. The gases also are produced to a considerable extent within the pelt and have a peculiar opening effect on the corium fibres. Moreover, if the drench has been used subsequent to puering or bating, the bran acts as a mechanical cleanser of the skin from the noxious products with which it has just been in contact. The following is a typical analysis of the drench acids :—

Lactic Acid . . .	0·7907	gm. per litre.
Acetic Acid . . .	0·2402	,, ,,
Formic Acid . . .	0·0306	,, ,,
Butyric Acid . . .	0·0134	,, ,,

If however, the temperature of the drench be too high, the proportion of butyric may very largely increase on account of a very vigorous butyric fermentation which is apt to take place, and in this case the skins are rapidly swollen to a considerable degree and may soon be irreparably ruined. If this by any chance occurs, the skins may be "pickled" by the addition of salt, which also checks the fermentation, or may be paddled in water to which borax, ammonia, or whitening is gradually added. This difficulty can be avoided and the activity of the drench much reduced by previously extracting some of the starchy matters from the bran by means of cold water. Conversely, the activity of the drench may be increased when

necessary by the addition of rye meal, pea meal, etc., to the bran when making up the liquor. In all cases it is desirable to keep the temperature below 35° C., and in some cases perhaps even 10° C. is not too low, but the time of the process must then be correspondingly increased. As with puering and bating, the requisite extent to which the process is to be carried can only be safely judged by experience in the treatment of any particular class of skin, but the skins should not be swollen till transparent, and should still be white and flaccid. If the drench is "working" too vigorously, the formation of the gases is apt to raise blisters on the grain, and, especially in the case of sheep skins, may thus separate the grain from the flesh and yield what is known as "pipy grain." The drench bacteria do not attack gelatin, so that if any damage occurs in this way it is probable that some injurious bacterium has been introduced from the puers or bates.

Chemical deliming agents have been suggested in endless numbers, but these are often merely acids which neutralise the caustic lime on the hide and are therefore more closely similar to the drench than to the puer or bate.

Boric (boracic) acid is now very widely used for this purpose and is popular for nearly all classes of leather. It has quite a mild effect on hide substance, and being difficultly soluble is harmless even in excess. It neutralises lime and in dilute solution forms calcium borates which are soluble in water. It is found in practice that by its use a beautiful silky grain may be obtained, in which respect it is in contrast with other deliming agents, and it is also found that it causes a decided improvement in colour during the early tanning liquors, and at the same time both quickens the tannage and prevents "drawn grain." For sole leather it is found very useful in removing the surface lime. It is also used to a considerable extent as a drench for bated hides, and being an antiseptic agent it stops all bacterial action. Light leathers often receive a bath of boric acid, even after drenching, to hasten the tannage and give a good grain and colour. It has been discovered that it is beneficial to keep the goods in motion in order to get a perfectly even action, so that skins are best treated in paddle, and "rockers" (p. 171) are found useful for the heavier goods.

Lactic acid is also found to be in certain respects a very suitable deliming agent. We have already noted that it is the chief active acid of the bran drench, and artificial drenches have been made up of similar compositions and found to be effective and rapid substitutes. A useful liquor of this nature consists of :—

Lactic Acid . . .	1·0 gm. per litre.
Acetic Acid . . .	·4 ,, ,,
Formic Acid . . .	·2 ,, ,,

It is observed, however, that such a reagent will not give the characteristic opening and inflating effect of the ordinary fermenting drench, because of the absence of any evolution of gases.

It may also be used alone in 0·2 per cent. solution as a deliming agent, and is best used in the paddle like the puer at a temperature of 30—35° C. Lactic acid is one of the natural constituents of "sour" tan liquors, in which it fulfils the same deliming function, and being one of the best plumping agents yet discovered, it is often added to "sweet" tan liquors to produce the requisite degree of acidity. It is made on a large scale by the "lactic fermentation" of sugar residues, and is put on the market in solution of about 45 per cent. strength.

Acetic acid, another product of the drench ferment, has also been suggested for deliming purposes, but the commercial article is apt to be very impure, and harsh grain has often resulted from its use.

Formic acid is now manufactured synthetically from caustic soda and carbon monoxide, and is obtainable in 60 per cent. solution. It is an effective deliming agent if used in very dilute solution, but if present in large quantity is liable to give a very rough grain.

Various inorganic acids have been suggested from time to time for deliming, but, except for special cases, they are not very extensively used. Sulphuric acid can be used if great care is taken and the acid added only gradually, but its lime salt is insoluble, and it has an exceedingly violent plumping action.

Hydrochloric acid has similarly been employed for pulling down dressing goods, but is objectionable for sole leather on

account of the formation of chlorides. Sulphurous acid is also effective, but must be used in excess to dissolve the insoluble calcium sulphite. Carbonic acid has also been used in a similar way. "Anticalcium," "C. T. bate," and similar preparations are mixed sulphonic acids derived from commercial cresols and aromatic hydrocarbons, and are more suitable as drenches than bates. They are good antiseptics, but are apt to swell somewhat.

Many neutral salts of weak bases have also been used as deliming agents, acting in a manner closely similar to the amido salts of the puer. Borax and ammonium chloride, sulphate, phosphate and oxalate have all been suggested, sometimes in addition to various weak acids. Common salt, as noted earlier, has a direct depleting action on the swollen skin, and when used along with even sulphuric acid may be very effective with goods for chrome tannage or in cases of "lime blast." An excellent preparation for any process of deliming skins is a good tumbling in soft warm water.

Practical Methods.—There is probably more variation in the methods of the deliming processes than in any other part of leather manufacture, but the following outlines represent some of the commonest modes of treatment :—

Sole butts should be kept as plump as possible, and hence all that is ever done is to neutralise the lime on the surface for the sake of colour, and to pass the goods immediately into tan liquors the natural acidity of which ("sourness") completes the neutralisation and keeps the goods well plumped. In yards where the tail suspender is very acid (see p. 170), the butts are merely washed with water. They are suspended in the water, which must be very soft (see p. 46), and either rocked or handled frequently for a few hours. Another way is to suspend in running water. The exact time depends upon the method employed and the acidity of the suspender liquors. This used to be quite the usual method for sole butts, but in those days the tan liquors were not so quickly worked down the yard, and in consequence had a good acidity (up to 10° lime water, see p. 154). The modern methods of working and the large proportion of "extract" (see p. 184) employed yields suspenders with comparatively little acid

(3° to 5° lime water), and hence it is now usual to give a short bath of some acid to the goods before passing them to the liquors. Boric acid is generally preferred for this purpose. The butts are rocked in a dilute solution for 4 or 5 hours, using 10 to 15 lbs. boric acid per 100 butts. This, in the author's experience, will remove all the surface lime and three-fifths of the total. If a hard water only is available the hardness should be "killed" with sulphuric acid before dissolving the boric acid, but an excess of the former should be carefully avoided. Good results can also be obtained with lactic acid. The acid used should be free from butyric acid and iron. About 12 lbs. commercial lactic acid should be used per 100 butts. Acetic acid has also been used successfully for this purpose, but is not popular. With better methods of manufacture, however, one can expect it to be increasingly used. Strong acids and mineral acids, such as formic acid, sulphuric acid and hydrochloric acid, can be quite well used if the principles of application are well understood. The solution must be dilute, the amount of acid used should never be in excess, and the quantity that is used should be gradually added in successive small quantities during the process. Shoulders and bellies are often merely washed in water, but it is better to give the former an acid bath. Scudding is desirable even in sole leather manufacture in order to ensure good colour, but the scudding should be light or bad weights will result. The operation should be carried out after deliming, when the surface of the hide is relaxed and scud loose; what is necessary can then be removed with little pressure.

Strap butts are sometimes lightly bated, a few hours being sufficient, and then given a bath of boric acid, using up to 20 lbs. of boric acid per 100 butts. More often in these days the bating is quite omitted and the goods simply delimed like sole leather. After scudding they are sent to the tan liquors.

Harness backs may be bated at 20° C. for 3 days, handling each day. Sometimes the thicker ones are softened mechanically by working with a graining tool. Any bate shaving next takes place, and the goods are suspended for 4 hours in

tepid water which contains 10 lbs. of boric acid per 100 backs. Scudding follows, and the goods then enter the tan yard.

In some yards the goods are not bated so much; they are put into the bate late in the afternoon and taken out next morning, or started in the early morning and taken out late at night. They are then delimed with 20 lbs. of boric acid per 100 backs.

A cheaper method still, now very common, is to have a longer liming, not less than 14 days, and to omit bating altogether. The goods are placed in a liquor containing 50 lbs. of boric acid per 100 backs and left until next day. They are then scudded, drummed with water to clean, rescudded, shaved if necessary, and sent to the tan liquors.

Dressing hides are generally bated at 25—30° C. but for some classes of goods 20° C. is sufficient. They are given 3 days in sets of 3 pits. When hauled the thicker ones are worked on the butt and neck to soften them. They are then sorted and scudded. Some tanners now drum them in tepid water (20—25° C.), again work them over the beam, and give them a bath of boric acid to complete the deliming, but others drum them straight away in boric acid, using 20 to 30 lbs. per 100 hides. This stops the action of the bate and gives good grain.

When lactic acid is used for deliming bated hides, 2 per cent. on the pelt weight of the commercial acid is taken. The deliming may be done in drums, but is preferably brought about in vats, a three-vat system being convenient. One-third of the total quantity of lactic acid is placed in each vat with sufficient water to keep the strength of the solution below 0·2 per cent. After mixing the solutions well, the rinsed hides from the bates are placed into each of the three vats successively for 8 to 12 hours, and then into water for 5 to 10 hours. They are then scudded by hand or machine, and sent to the tan house. Where a soft grain is desired the goods are placed in a large paddle with weak boric acid, and paddled 2 to 5 hours. The liquor in the first vat contains now no free acid and is run away. A new liquor is made in its place with fresh water and lactic acid, and the next pack goes first into the second vat, then into the third, and finally into the new liquor.

E. I. kips are rinsed and scudded after fleshing and then bated for 3 to 5 days at about 30° C., handling frequently. About one bushel of hen-dung is used for every 100 skins. After rinsing through water, the skins are sometimes bate-shaved, and bate-grained, and are then lightly drenched with 6 per cent. of bran on the pelt weight, scudded again or merely rinsed and placed in the tan liquors. Some bating is almost absolutely necessary for this class of goods in order to obtain the desired softness in the finished article. Lactic acid, however, is employed to some extent to complete the deliming after bating, *i.e.*, as a substitute for the drench. The skins are put into plenty of warm water (30—35° C.) in a paddle and 2 per cent. lactic acid on the pelt is diluted considerably and added gradually over a period of 2 to 3 hours. There should be at least three batches, and in this case not less than 20 minutes should elapse between each addition. The solution, moreover, must never be stronger than 0·2 per cent. One of the chief differences between drenching and chemical deliming is that in the former the acid is gradually produced and neutralised. In the latter, therefore, the more gradually the acid is added the greater the approximation to the conditions of drenching.

Calf skins for "shoe calf" (vegetable tannage) are treated very much in the same way as kips, but are bated more lightly and are preferably drenched. From 2 to 3 days in bates, and 6 per cent. of bran for drenching are quite sufficient.

For book-binding leathers the skins are severely bated. Five days at 30° C. is sufficient. Occasionally book-binding calf are puered. They are bate-shaved and drenched with 8 to 9 per cent. of bran.

For chrome calf neither bating nor puering is either necessary or desirable. The nature of the chrome tannage demands the full amount of hide substance in the skins for obtaining the requisite fullness. As, moreover, the tanning material is all inorganic, there would seem no obvious reason for deliming at all. This is certainly true with regard to the two-bath process (p. 213), the first bath of which will completely and effectually delime the goods by means of its free acid, hydrochloric or chromic. Sufficient acid, however, should be

added to the bath to compensate for this if the goods are not delimed. By this method the skins would be rinsed, scudded, rinsed again and inserted straight into the chroming bath. The one-bath process (p. 219) almost demands a surface deliming, with lactic acid for example, to avoid the formation of calcium sulphate on the grain, but otherwise no deliming would seem to be necessary. It is nevertheless quite common to delime calf skins for chrome tannage by puering, and this undoubtedly makes it easier to obtain that silky feel on the grain which is so much desired for "box calf" and "box sides." A common method is to delime with acids and drench lightly. Four parts of formic acid are mixed with one part of lactic acid (each being of about 40 per cent. strength), and about a pint of the mixture is used for every 100 lbs. of pelt. The skins are first rinsed and scudded, and then paddled for half an hour in water to get rid of the excess of lime. They then enter the deliming paddle, which contains half a pint of the acid mixture per 100 lbs. pelt. After half an hour's running the other half pint is added and the paddling continued until the skins, when cut and tested with phenol phthalein, show only a very thin streak of red. The skins are then rinsed through water, drenched overnight at 25—30° with 6 per cent. bran on the pelt weight. After branning or rinsing they are ready for tanning. Another method to is drum with tepid water and delime by drenching with 10 per cent. bran.

It is also common to place calf for chrome work into a solution of 5 per cent. of potash alum and 5 to 10 per cent. salt, before placing them in the chrome liquors. Often also the undelimed or merely surface delimed skins are completely delimed by this bath. It is extremely doubtful, however, whether this has any beneficial effect for either one-bath or two-bath leathers.

For "calf kid" the skins are plumped in fresh limes for a few days after unhairing and fleshing, and afterwards gradually delimed by steeping in a series of waters softened by the addition of some of that previously used for the same process. No dung is used, but a certain amount of bacterial action undoubtedly takes place. The goods are next drenched in 3 to 4 per cent. bran.

Sheep skins, whatever their destiny, have to be "degreased" some time during the process of manufacture, and this is often brought about in the limed state by pressing out the grease from the warm skins. The skins are placed one by one into a hydraulic press with a layer of sawdust or bran between each and an iron plate between every hundred. Usually about 1,000 are put into the press each time. The pressure is applied very slowly indeed or the skins are ruined, being at this stage very liable to damage. Most of the grease is removed on pressing in this way, and the rest comes out in puering and scudding. Tanned skins are degreased by extracting with solvents. They are drummed or churned with benzine, to which acetone is often added; the vessels are kept carefully shut, and the solvent is recovered for subsequent use.

For "skivers," sheep skins are always split in two by machine before degreasing, giving grains (the "skivers"), and fleshes, which latter are often given an oil tannage and made into chamois leather (p. 247). After splitting the grains are degreased, thoroughly puered at 30° C. for about three hours in paddle or drum, and then worked over the beam to remove scud. They are next drenched for 2 to 3 days at 20° C., and, after again working over the beam, are rinsed and sent to the tan house. The fleshes are given a further thorough liming after splitting, using fresh limes, then drenched to remove caustic lime, and allowed to drip dry for oil dressing.

For "roans" the skins are degreased and puered and scudded as above, and drenched overnight in 10 per cent. of bran at 30—35° C. After branning they pass to the tan house.

For "roller leather" the skins are machine-fleshed, short-haired, and are then ready for puering. In many of the smaller yards dog-dung is still used for this, but in the larger works either erodin or merely some weak deliming acids are used instead for pulling down. The skins are then drenched with bran in paddle pits, the paddles of which run only intermittently. The skins are then thoroughly scudded and pass into the tan liquors.

For "basils" sheep skins are sometimes puered, but usually

bated for two days at 25—30° C. with constant handling. After scudding and drenching they are again worked over the beam and sent to the tan house. Another method is to delime with acids instead of bating. A mixture of four parts of formic and one part of acetic acid is used. After fleshing and short-hairing they are washed in paddle with water at 33—35° C., and the extent of this washing determines the amount of acid to be used in deliming. The acid "bate" is prepared in a paddle with clean water at 30° C., to which one quarter of a pint acid mixture has been added per 100 skins. The skins are paddled 15 minutes, and another quarter of a pint of acid is added. One or two thicker skins are now tested with phenol phthalein, and if any red shows a further portion of acid is added and the paddling continued. This is repeated until the deliming is just complete, but care must be taken to avoid excess of acid or the skins will swell. The goods are now rinsed through water and drenched overnight with a half bushel of bran per 100 skins, made up as usual to be 30° C. Next morning the skins are removed, washed, scudded if necessary, and sent to the tan house.

For chrome work, imitation glacé, etc., the skins must be degreased and are better puered. They are thoroughly scudded and then delimed by drenching with 6 per cent. bran or by means of lactic acid. They are also often delimed by pickling (see below) in acid and salt, and in some large works pickled skins are dried out for sorting.

Pickling consists in treating the skins with common salt and a small quantity of sulphuric acid (or of other acids), which preserves the skins temporarily. The process is particularly useful where the skins are to be exported. Acid is of course readily absorbed by pelt, which swells up under its influence. The addition of common salt to the liquor, however, totally prevents any swelling and, indeed, pulls down the skins, but does not hinder the absorption of acid, and hence skins treated in this way undergo a temporary tannage into a kind of "white leather." Pickled skins can at any time be "depickled," and then tanned by the ordinary methods. Many recipes have been given for pickling in one bath, but there is little doubt that where the skins are to be

thoroughly pickled and kept for some time in this state, the best method is to finish up in a saturated salt solution.

The method given by Procter, based on theoretical as well as practical considerations, is the best. It is a two-bath process. The skins are first paddled for 30 to 35 minutes in the "rising solution," which is a 0·75 per cent. solution of sulphuric acid containing also 8 per cent. of salt to keep the swelling within limits. The amount of acid in this bath should be kept as nearly constant as possible for each pack of skins, being restored each time a pack comes out. About 15 cc. of N/1 NaOH should always be required to neutralise 100 cc. of the bath to phenol phthalein. Some salt is also absorbed and removed by the skins, and the strength of this should also be kept approximately constant. This is done with sufficient accuracy by keeping the specific gravity of the liquor at 1·065, which is readily ascertained by means of the Barkometer (65°) (see p. 155). The skins are now stirred in the "falling solution" for several hours, until the thickness of the skins is quite reduced. This bath is a saturated salt solution containing excess of salt, the strength therefore being quite unaffected by any dilution due to the added skins. The skins are then either dried out or kept in contact with a saturated salt solution. Pickled skins must be rigidly kept away from water, as in contact with it they both swell violently and stain badly. Depickling may be brought about by wetting back the skins in a 10 per cent. salt solution to which an excess of whitening has been added. The salt restricts the swelling until the acid diffuses out and is neutralised by the calcium carbonate. The skins can then be washed and tanned by any of the ordinary methods. Other alkalies may be used besides whitening for depickling; borax, sodium carbonate and bicarbonate and other sodium salts of weak acids are effective, but should be carefully added to the solution so that no excess is obtained. Pickled skins may also be given a vegetable tannage without depickling if salted liquors are used.

It has been pointed out by the Committee of the Society of Arts on book-binding leathers, that the action of even small quantities of sulphuric acid has a considerable deleterious influence on the permanence of book-binding and furniture

leathers, so that it is becoming increasingly common to adopt the suggestion of Seymour-Jones and substitute formic or acetic for sulphuric acid in pickling. By this method the skins after deliming and drenching are paddled in a 0·25 per cent. solution of formic acid for a time, and then left 24 hours, and are afterwards transferred to a saturated salt solution for 24 hours

For chrome work pickling is more of a deliming process and preparatory treatment for tannage, and therefore can be quite well carried out in one bath. The quantities are usually reckoned on the pelt weight; 100 lbs. pelt require 2 to 4 lbs. hydrochloric or sulphuric acid and 8 to 10 lbs. of salt dissolved in 15 to 20 gallons of water. The goods are drummed in this for perhaps 15 minutes, during which the diluted acid is slowly added, and then allowed to stand for a few hours.

Sheep skins are particularly difficult to deal with in the wet work, largely no doubt on account of their greasy nature, but partly also because they are somewhat liable to bacterial and mechanical damage, and because the animals are subject to various skin diseases, all of which make it a matter of considerable difficulty to prepare leathers of good appearance and quality. The following are some of the common sheep skin troubles. "Colt" is a spring disorder in the animal resulting in a curdling in the fat glands, which causes lime soaps to be fixed in the skin even till after tannage. "Cockle" is a somewhat mysterious sheep skin disorder which occurs when the animal has a heavy coat of wool. Pimples appear which are full of pus or matter. This disease also appears in spring, but soon disappears when the animal is shorn. "Lime speck" is a trouble which occurs when the skins have been too long in contact with lime paste, or occasionally when they have been too long in the lime liquors. It appears as a spot or even as a circle up to a quarter inch in diameter, and is probably due to the deposition of some calcium compound by one of the putrefactive bacteria. "Pin holes" are mostly found in skivers and are due to over-sweating, but sometimes to over-liming. They are minute spots which are often not noticeable unless the light is appropriately reflected. "Pitted" is a

name given to a very similar appearance but with rather larger holes. It is caused by leaving the skins too long in the soaks, especially in warm weather. The last three defects mentioned are of course cases of bacterial damage.

Lamb and kid skins for glove leathers are puered at 18°—20° C. for some hours. About 1 or 1½ pailfuls of dung paste are sufficient for 200 skins. The process should be complete in 2 to 3 hours for these skins, but may take 12 to 14 hours for strong skins, paddling 10 minutes each hour for 5 to 6 hours, and then allowing to lie undisturbed. After careful scudding they are drenched at 35° C. for 1 to 3 hours.

Goat skins for morocco leathers are puered at 27—30° C., afterwards worked over the beam, rinsed, and again worked over the beam. They are then drenched overnight at 30—35° C. with 10 per cent. of bran. After scudding they are forwarded to the tan house.

For chrome glacé goat the skins should, for the best leathers, be thoroughly puered in order to obtain a smooth grain, and are then usually drenched at 15—20° C. for 2 to 3 days; they are then rinsed and placed in the chroming bath. It is usual in many of the large American factories to omit the drenching altogether. Many processes have been devised to do away with puering for this class of chrome leather, but without complete success. Clean skins and a plump, soft, fine-grained leather are said to be obtained, however, by the following method. The skins are washed in warm water, and puered in the ordinary manner at 30—33° C. for three-quarters of an hour, till the skins just begin to fall; they are then rinsed through water and scudded. The deliming process is now completed by paddling in a solution at 30° C. in which 3 lbs. of calcium chloride and a half pint of a mixture of four parts formic and one part lactic acid are dissolved for every ten dozen skins. The skins are then rinsed through water and placed in the chroming liquor. Another method, only suitable for cheaper classes of goods and poor skins, is carried out as follows: A paddle liquor is made up at 30—35° C. as above with a half pint of the formic-lactic mixture. The skins after washing in warm water are paddled in this twenty minutes, and more acid is gradually added until the skins are just delimed. They are

then washed through water, and drenched overnight with a half bushel of bran per ten dozen skins. Next morning they are washed, scudded, and sent to the tan house. This process is apt to give a rather harsh grain, doubtless an effect of the acids used.

Seal skins are heavily puered at about 35° C. for about three hours. They are then scudded by machine or by hand, and drenched overnight at 20° C. with 10 per cent. of a mixture of bran and pea meal. They are then sent to the tan yard.

Chemical Control of Deliming Processes.—Little can be done in the case of bating and puering, as already pointed out, but the acidity of the drench liquor may be determined by titrating with N/10 caustic soda and phenol phthalein. Boric acid alone gives no definite end point with phenol phthalein, but can be accurately estimated in the presence of glycerin. To 50 cc. of boric solution (if about 1 per cent.) add 30 cc. of *neutral* glycerin and titrate, with N/10 caustic soda and phenol phthalein. Each cc. used corresponds to 0·062 gm. H_3BO_3.

Lactic acid is apt to contain some anhydride, so that it is necessary to boil with a measured excess of N/10 caustic soda and titrate back with N/10 acid. The total acid may thus be determined, and the first appearance of the pink colour in direct titration gives a means of estimating the anhydride also.

CHAPTER IX

THE TANNINS

Although the term "tanning" now includes the treatment of hides with mineral salts, oils and aldehydes, as well as with infusions of the vegetable tanning materials, the term "tannin" (or tannic acid) is still restricted to these latter, and is used as a class name for the essential constituents of them. The tannins may therefore be defined as a group of organic compounds which can be extracted from many vegetable materials by water, giving infusions which all possess, the property of converting the hide tissue of animals into an imputrescible and permanent material known as leather. A similar reaction occurs when the tannins are added to a dilute gelatin solution, a curdy precipitate of "amorphous leather" being obtained. A delicate test, therefore, for the presence of tannin in solution is to add two drops of a 1 per cent. gelatin, 10 per cent. salt solution to the liquor, a turbidity being produced if the solution contains more than one part of tannin in 100,000. The tannins are also all precipitated by a solution of basic lead acetate, and many of them more or less completely by solutions of many metallic salts, alkaloids and basic colouring matters. In dilute solutions ferric salts give dark colorations. Alkalies rapidly cause the tannins and many associated compounds to darken, oxidation taking place, and a deep red colour is also obtained by the addition of potassium ferricyanide and ammonia. The tannins are soluble in water, alcohol, acetone and ethyl acetate, but insoluble in benzene, chloroform, carbon disulphide, petroleum ether, dilute sulphuric acid and *pure* ether, though some quantity may be dissolved by ether containing water or alcohol. They all contain only carbon, hydrogen and oxygen, and belong to the aromatic division of

organic compounds, being derivatives of the dihydric and trihydric phenols and their carboxyllic acids. Our knowledge of their chemical constitution, however, is as yet very incomplete, and this is chiefly due to the impossibility of obtaining these bodies in a pure condition. They are all uncrystallisable and non-volatile in air or steam. They are very unstable, and hence in many cases are confused with their decomposition products. Most plants also contain mixtures of more than one tannin, and the impossibility of separation makes the evidence of experimental investigation very inconclusive.

The methods of purification of the tannins are thus very limited, and as each tanning material contains very different soluble non-tannin bodies, no general process of purification can be described. The following methods, however, with modifications according to the material, have been found useful either alone or in conjunction.

Fractional solution in different liquids is perhaps the most generally useful method. The material may be extracted with alcohol or acetone and the solution evaporated to dryness, the later stages under reduced pressure. An aqueous infusion is now made, and insoluble impurities (phlobaphenes, resins, etc.) filtered off. The filtrate may now be agitated with ethyl acetate which is immiscible with water and which takes up most of the tannin. This process may sometimes be assisted by the presence of common salt. The ethyl acetate solution of the purified tannin may now be evaporated to dryness. Water, of course, may be used for the extraction, and the clear infusion treated with salt and ethyl acetate direct. The employment of ether is also extremely valuable at many stages of these processes, various impurities (gallic acid, etc.) being soluble in it. Being only partially miscible with water, it may be either shaken with aqueous solutions or used upon the dry tannin at any stage.

Fractional precipitation of aqueous solutions by means of lead acetate, the middle fractions only being taken, gives the lead salts of the tannins. These may be decomposed by an insufficient quantity of dilute sulphuric acid or by passing sulphuretted hydrogen through water in which the lead salt is

suspended. The filtrate contains the purified tannin and may be evaporated to dryness. It is often uncertain, however, whether the tannin has not been changed by this process.

Organic derivatives of the tannins, such as the crystalline acetyl compounds, have been used for purification purposes,[1] but these are not so reliable as the less drastic methods.

The classification of the tannins is as yet very imperfect owing to our ignorance of their chemical constitution. When heated carefully to about 200° C. all tannins yield either pyrogallol or catechol, and occasionally phloroglucol, together with other products, and this forms the basis of their division into pyrogallol tannins (tannins derived from pyrogallol) and catechol tannins (tannins derived from catechol), which division is further justified by other marked differences between the two groups. These are summarised in the following table :—

Test. (*Use dilute aqueous solution.*)	Pyrogallol tannins.	Catechol tannins.
Boil with dilute sulphuric acid.	Yellow ppt. of ellagic acid, insol. in cold alcohol and hot water (not given by some).	Red ppt. of phlobaphenes, soluble in cold alcohol and hot water.
Add iron alum solution.	Blue-black colour.	Green-black colour.
Add bromine water.[2]	No ppt.	Precipitate.
Add diazo benzene chloride.[3]	No ppt.	Precipitate.
Add to one drop of solution conc. H_2SO_4.	Brown or yellow colour.	Crimson colour.

The coloration tests are naturally not completely satisfactory in the presence of mixtures of tannins from both groups, but the precipitation tests are still reliable. Another significant difference between the two groups is that the

[1] Vournasos, "Le tannin de la noix de galle, sa constitution," Baillère et Fils, Paris, 1903.
[2] Procter, J.S.C.I., 1894, 488.
[3] Nierenstein, Collegium, 1906, 376.

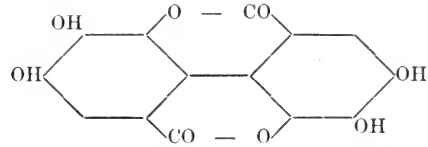
catechol tannins invariably contain about 60 per cent. of carbon, whereas the pyrogallol tannins contain only about 52 per cent.

Pyrogallol tannins and associated substances. — *Pyrogallol* (*pyrogallic acid*, 1 : 2 : 3 *trihydroxy benzene*) $C_6H_3(OH)_3$, the parent substance of this group, is a trihydric phenol which melts at 132° C. and sublimes at 210° C. It is soluble in water, alcohol, ethyl acetate, ether and acetone, but insoluble in chloroform and petroleum ether. Its aqueous solution gives a red colour with ferric chloride, and a blue colour with ferrous sulphate which is turned red by acids and restored by ammonia. In the presence of alkalies oxygen is very rapidly absorbed and the mixture darkens quickly. It does not precipitate gelatin, but reduces the salts of silver, gold, platinum and mercury, and also Fehling's solution. It is precipitated by lead acetate and some other metallic salts. Many oxidising agents cause it to yield purpuro-gallin, a napthalene derivative. Metagallic acid is formed by heating rapidly to 250° C. This is a black amorphous substance soluble in alkalies but not in water, and is also formed from gallic and gallotannic acids when treated in a similar way.

Gallic acid (3 : 4 : 5 *trihydroxy benzoic acid*), $C_6H_2(OH)_3COOH$ is found associated with many pyrogallol tannins, and is formed by the hydrolysis of gallotannic acid by acids, alkalies or ferments. It is difficultly soluble in cold water but readily in hot, from which it crystallises on cooling in pale yellow needles containing a molecule of water of crystallisation. It is soluble in alcohol and ether, and by the latter may be removed from aqueous solution. When carefully heated to 210° C. it loses carbon dioxide, and yields a sublimate of pyrogallol, but if raised quickly to 250° C. metagallic acid is formed. Rufigallic acid (hexa-oxyanthraquinone) is obtained by heating with concentrated sulphuric acid to 140° C. and diluting with water. Alkaline solutions of gallic acid darken and absorb oxygen. Ferric chloride gives a blue colour, and pure ferrous sulphate a white precipitate which rapidly darkens. Lime water gives a precipitate which turns blue by oxidation (ctr. pyrogallol). Potassium cyanide gives a red colour, and sodium arsenate a

green colour. A hot solution reduces potassium permanganate, and salts of silver and gold, but not Fehling's solution. It does not precipitate gelatin but is absorbed to a considerable extent by hide powder[1] (p. 147).

Ellagic acid ("bloom") $C_{14}H_6O_8$ is a double lactone of a hexa-hydroxy-diphenyldicarboxyllic acid, and has the following constitution[2] :—

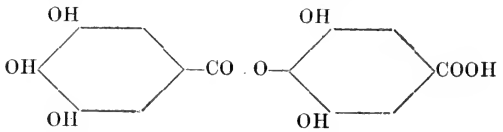


It is obtained by the decomposition of ellagitannic acid as a yellow amorphous powder, and is therefore yielded by any material containing this tannin either by the action of acids or ferments. It may be purified by crystallisation from pyridine or absolute alcohol. It is insoluble in cold alcohol or hot water, but soluble in alkalies, being decomposed by hot caustic potash solution and further still by fusion with potash, the lactone groups opening up and the carbonyl groups being eliminated. It may be prepared from gallic acid by oxidation of its 10 per cent. solution in acetic acid with potassium persulphate and a little sulphuric acid, and pouring into water. It is a feeble colouring matter. Nitric acid, containing nitrous acid, gives with it a crimson colour. Flavellagic (hydroxyellagic) acid $C_{14}H_6O_9$, catellagic acid $C_{14}H_6O_6$ (a dihydroxy compound) and metellagic acid $C_{14}H_6O_5$ (a monohydroxy compound) are very similar in properties and are obtained in similar ways.

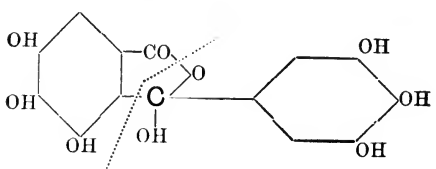
Gallotannic acid (*digallic acid*) $C_{14}H_{10}O_9$ is the principal tannin of oak galls and of sumac. It also occurs with ellagitannic acid in many other materials (myrobalans, divi-divi, etc.). Its chemical constitution has received more attention than has been given to any other tannin, but is still not satisfactorily elucidated. Many syntheses of gallotannic acid have been claimed, but doubt has been thrown upon

[1] Parker and Bennett, J.S.C.I., 1906, 1193.
[2] A. G. Perkin, J. C. S. 1905, LXXXVII., 1412, 1418, 1426, and LXXXIX., 251.

them all. It is usually accepted to be an anhydride of gallic acid, and the most commonly used formula is the following[1]:—



There is some evidence, however, for the view that it exists in the plant originally as a glucoside, and it has been pointed out, moreover, that the purified tannin is optically active and dextro-rotatory, so that many other formulæ containing an asymmetric carbon atom have been suggested, amongst which that of Dekker may be mentioned here:—



The presence of a carboxyl group is doubtful, and the number of hydroxyl groups in the molecule is as yet indeterminate. Various acetyl and benzoyl derivatives have been described, but their composition seems to vary somewhat widely.

Commercial gallotannic acid is a buff-coloured powder with a characteristic odour, and containing varying quantities of gallic acid, glucose, starch, etc. It is somewhat hygroscopic and contains usually 10 to 12 per cent. of moisture. When hydrochloric or sulphuric acid is added to a strong solution a white precipitate is obtained, which when boiled with excess of acid is completely converted into gallic acid. Ferments and warm alkalies (in the absence of oxygen) accomplish the same hydrolysis. Ellagic acid is not obtained from gallotannic acid under any of these conditions. The aqueous solution gives precipitates with gelatine, various alkaloids and other organic bases, with lead nitrate, lead acetate and acetic acid, ammoniacal copper and zinc solutions and with tartar emetic

[1] Vournasos (see footnote p. 115).

and ammonium chloride, and by these reactions may be distinguished from gallic acid, from which, however, it cannot be quantitatively separated. It gives white precipitates with baryta and lime water[1] which rapidly oxidise and turn blue, purple, and finally black.

Ellagitannic acid is a pyrogallol tannin often occurring naturally with gallotannic acid. It occurs most plentifully in myrobalans, valonia, divi-divi and algarobilla. Almost nothing is known of its constitution, but its presence is always recognisable by the formation of ellagic acid (bloom) from its aqueous infusion, by the action of ferments as in practice, or by hot dilute mineral acids. The yield of bloom may be taken as a measure of the quantity of ellagitannic acid.

Oakwood tannin ($C_{15}H_{12}O_9 \cdot 2\,H_2O$?),[2] which is used extensively in practice in the form of oakwood extract, has been thought to be a methyl derivative of gallotannic acid, but it is probably a mixture, and certainly is capable of yielding a considerable quantity of bloom.

Babool tannin (pods) is a pyrogallol tannin which does not give a precipitate with lime water.

Chestnut wood, divi-divi and algarobilla contain pyrogallol tannins which resemble both gallotannic and ellagitannic acids.

Catechol tannins and associated compounds. *Catechol (pyrocatechin, 1 : 2 dihydroxy benzene)* $C_6H_4(OH)_2$ the basis of the tannins of this group, is a dihydric phenol which melts and sublimes at 104° C. It is soluble in water, alcohol and ether. It gives a dark green colour with a few drops of ferric chloride solution, which is turned red by alkalies and restored by acids. It does not precipitate gelatin or alkaloids, but darkens in alkaline solution. Silver salts are reduced by it in the cold, and Fehling's solution on heating. It is precipitated by lead acetate (ctr. resorcinol and quinol).

Protocatechuic acid (3 : 4 dihydroxy benzoic acid) $C_6H_3(OH)$, COOH is a decomposition product of the catechol tannins

[1] Procter and Bennett, J.S.C.I., 1906, 251.
[2] Böttinger, Ber. XX., 1887, 761—766.

catechins and phlobaphenes. It crystallises from hot water in white needles containing a molecule of water of crystallisation. It strongly resembles gallic acid in its properties and reactions, but its barium and calcium salts are more soluble.[1] Vanillic and iso-vanillic acids are methoxy derivatives.

Phloroglucol (*phloroglucin* 1 : 3 : 5 *trihydroxy benzene*) $C_6H_3(OH)_3$ is an isomer of pyrogallol. It melts at 220° C. and sublimes. It is soluble in water, alcohol and ether. When pure it gives no colour with iron salts and is only precipitated by basic lead acetate. Bromine water gives a white precipitate of the tribrom derivative. When a deal shaving is moistened with its solution and concentrated hydrochloric acid added, a deep violet colour is formed which is not given by catechol and pyrogallol. It is obtained from some catechol tannins by dry distillation, but more usually on fusion with potash.

The catechins are thought to be the parent substances of the catechol tannins, which are supposed to be their first anhydrides. They are white crystalline bodies occurring naturally with the catechol tannins. They are sparingly soluble in cold water, but freely in alcohol, ether and hot water. Aqueous solutions give precipitates with lead acetate, mercuric chloride and albumin, but not with gelatin, alkaloids or tartar emetic. When heated with dilute mineral acids they are first converted into tannins and afterwards into phlobaphenes, probably by dehydration in successive steps. They are often deposited as "whites" on the sides of pits containing gambier liquors.

Gambier catechin, $C_{15}H_{14}O_6 \cdot 4\,H_2O$, has been thoroughly investigated by Perkin.[2] It melts at 176—177°, gives the deal shaving reaction for phloroglucol a green colour with ferric chloride and yields acetyl, benzoyl and azobenzene derivatives which indicate five hydroxyl groups.

An isomer has been isolated from the same material, but with no water of crystallisation and melting at 235—237° C., but otherwise similar in properties.

[1] Procter and Bennett, J.S.C.I., 1906, 251.
[2] A. G. Perkin, J. C. S., LXXXI., 1892, p. 1160.

Acacia catechu yields a catechin melting at 204—205° C., which is also isomeric and similar in properties to the above.

The phlobaphenes or *reds* are the condensation products (anhydrides) of the catechol tannins, from which they are derived by the continued boiling of solutions of these tannins or by boiling in the presence of mineral acids. They are usually found to some extent associated naturally with the parent tannin. They are sparingly soluble in cold water, but freely in alcohol and hot water. They are soluble in dilute alkalies, alkaline carbonates, and in sulphites, borax, etc., and have been thereby made available for tanning. Each catechol tannin yields a series of these "reds," the solubility of which decreases as the degree of condensation and dehydration increases. The more soluble members are the "difficultly soluble tannins," which form the principal colouring matters of the materials containing them, and which combine with hide to form leather. The more insoluble members form the red sediment often found in tan pits. On fusion with caustic potash they all yield protocatechuic acid, and some yield phloroglucol.

Catechutannic acid is the name given to the catechol tannins of gambier, cutch, kino and other plants. It appears to be formed by the condensation of the catechins, and yields bromine derivatives containing about 50 per cent. of bromine. It probably represents several chemical individuals, of which the tannin of gambier is the least astringent and combines most loosely with hide fibre.

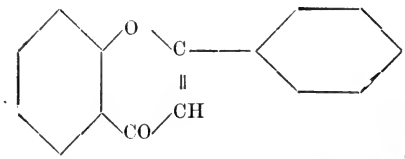
Quercitannic acid is the principal tannin of oak bark, which also contains the associated phlobaphene. It contains 59·8 per cent. carbon, but the evidence for its constitution is somewhat contradictory. Its bromine derivative contains 28·4 per cent. of bromine.

Quebrachotannic acid is the principal tannin of quebracho wood and extract. It contains phloroglucol and also readily yields phlobaphenes by condensation; its bromine derivative contains about 43 per cent. of bromine.

The catechol tannins of mimosa and chestnut barks resemble quercitannic acid.

The flavones are natural colouring matters found associated

with the tannins. They are hydroxy derivatives of flavone, of which the constitution is as follows:



Quercetin, myricetin, fisetin and morin are some of the principal members.

It is noteworthy that phosphorus oxychloride, arsenic acid, sulphuric acid, aldehydes, and the halogens, all act upon the higher phenols and their carboxylic acids to form compounds which have many of the reactions of tannins.

CHAPTER X

THE VEGETABLE TANNING MATERIALS

The tannins described in the previous chapter are very widely distributed in the vegetable kingdom, but exist in very varying quantities in the different plants. A vast number of plants contain a certain amount of tannin in some of their parts, but only a limited number contain sufficient to be of commercial importance in the leather industry, and it is with these materials only that this chapter will in any way attempt to deal. The tannins are found in almost all parts of plants, and the vegetable tanning materials may therefore be barks, wood, twigs, leaves, fruit, or even excrescences (*e.g.*, galls). Generally speaking, barks and fruits are found to possess the greater tannin strength in trees, but the wood, though containing less tannin, is often found to be a cheaper source. Hence it is that fruits are usually imported in the natural state, whilst wood is converted into "extract" by the careful evaporation of its aqueous infusion.

As so many different parts of various plants contain tannins of commercial importance, it is outside the scope of this work to give any account of the structure of these plants, and the reader is therefore referred to works on botany. It should perhaps be pointed out, however, that in barks the tannin is contained chiefly in the bast layer which lies just under the epidermis, in roughly cubical cells with rather thick walls. These often contain starch granules of characteristic forms, which can be examined microscopically by staining sections with iodine solution. Tannin is similarly detected by staining with an alcoholic solution of ferric chloride. The "reds" and dark colouring matters are usually contained in the outer and dead part of the bark, which as a rule contains little tannin.

Although it is known that the natural tannins are often

mixtures of more than one chemical individual, and that different tannins occur in different parts of the same plant, it has been shown, on the other hand, that it is usual to find one of the two main groups of tannins in predominance, so that the natural materials generally yield infusions which contain chiefly pyrogallol tannins, or which consist almost entirely of catechol tannins. As the difference between these two groups is practical as well as theoretical, this method of classification has been adopted also in this chapter. Broadly speaking, the group of pyrogallol materials produce rather soft and porous leathers when used alone (though valonia is an exception), but yield "sour" liquors and plump well on account of the fermentable sugars naturally associated with them, which yield various organic acids. Many of them also deposit "bloom" (p. 117). The catechol group, on the other hand, deposit "reds" (p. 121), which often occur as sediment at the bottom of the pits; and some yield "whites," a crystalline deposit of catechins (p. 120) on the sides of the pits. This class of materials often contains little or no sugar, and hence with catechol tanning materials alone hides cannot usually be satisfactorily tanned. For most leathers it is desirable to combine the two classes, but if the catechol tannins are alone employed it is necessary to resort to an artificial acidification of the liquors[1] and possibly also a "raising" of the pelt with acids.

Pyrogallol Tanning Materials.

Valonia is the calyx or acorn cup of the Turkish oak (*Quercus aegilops*), though probably obtained also from other species (*Q. macrolepis*, *Q. graeca*, etc.). It grows extensively in Asia Minor and Greece. The fruit in the former district ripens in August, and is gathered and forwarded to Smyrna, which gives rise to the term "Smyrna valonia." This is stored at Smyrna in special chambers, in layers of about one foot deep, until dry. The drying process is fermentive and in a few weeks the acorn, which contains but little tannin, falls away from the cup. The cups are then sorted by hand; the largest and finest cups being exported to Trieste and used

[1] Bennett, J.S.C.I., 1908, 1193.

in Austria, Germany and France; the second quality and much of the remainder comes to England.

The "Greek valonia" is obtained from many parts of the Grecian Archipelago as well as the mainland. The best quality is obtained when the fruit is still immature and the acorn well enclosed. This is known as *camatina* if the acorn is quite covered, and as *camata* if slightly exposed. It gives excellent colour, and is therefore used in dyeing. The second quality (*rhabdisto*) is beaten off in September and October, and the *charcala*, which falls after the first rains, is valueless and not collected. The tannins contained are a mixture of both groups, but chiefly from the pyrogallol section, including a

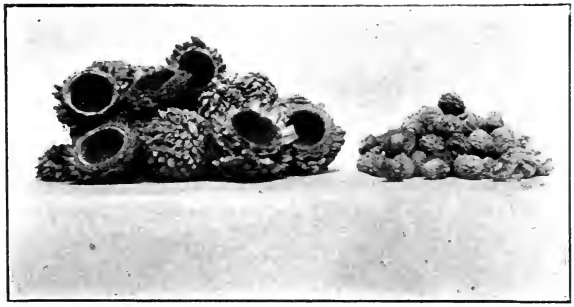


FIG. 33.—Smyrna and Greek valonia (*camata*).

considerable proportion of ellagitannic acid (p. 119). This makes the material extremely suitable for the tannage of sole leather goods, the deposition of bloom in the material making a firm compact leather of good weight. If the bloom be allowed to deposit before use tannin is of course lost, but a tannage very suitable for dressing leathers is obtained, and in conjunction with gambier and other materials, it is often thus used. The relative value of Greek and Smyrna valonia to the tanner has been investigated by Parker and Leach[1] with interesting results. Samples of average quality were taken with great care and submitted to an analytical investigation.

[1] J.S.C.I., 1903, 1184.

The cup and beard were analysed separately and also together, taking two-thirds cup and one-third beard to represent the bulk. The analyses are given in the following table, together with the tintometer (p. 154) results :—

Material.	Tannin.	Non-tannins.	Insoluble.	Water.	Red.	Yellow.
Smyrna valonia .	32·43	12·50	43·07	12·00	1·6	5·6
,, cup .	30·99	12·79	44·12	12·10	1·7	4·6
,, beard .	43·61	14·45	29·93	12·01	1·2	4·1
Greek valonia .	32·07	12·96	42·97	12·00	1·5	5·0
,, cup . .	27·37	12·92	47·71	12·00	2·0	6·7
,, beard .	41·03	13·96	33·01	12·00	1·3	4·4

This shows a slight superiority in strength and colour on the part of the Smyrna variety. The bloom-yielding properties were also investigated, and it was found that in each case about 75 per cent. of the total was deposited in a fortnight. The Smyrna valonia yields a greater amount than the Greek valonia, and in each case the cup more than the beard. It was found also that the Greek variety produces more acid than the Smyrna, and in both cases the acid is more quickly formed from the beard.

The valonia tannins have only moderate affinity for hide substance and penetrate it very slowly, but the material has excellent weight-giving properties, and leather tanned with it offers considerable resistance to water. The internal deposition of bloom accounts for the last two properties.

Myrobalans[1] is the name given to the dried fruit of the Indian *Terminalia chebula*, though other species are sometimes used. These trees grow to a height of 40 to 50 ft., and are valuable also for their timber. The nuts are about the size of a pigeon's egg, but some are elongated and wrinkled. As they ripen on the trees certain of these are

[1] Sometimes called "myrobalams," "myrabolams" or even "myrabs."

picked by hand before the sun has had time to darken them in colour. These form the "picked" varieties, and usually fetch a higher price in the market. Afterwards, as the fruit ripens, the trees are knocked or shaken and the fruit falls to the ground and is collected. On reaching the warehouse it is sorted by hand according to colour into "No. 1," "No. 2," and sometimes "No. 3" varieties. It has been shown that the riper the fruit the greater is the tannin strength and the

FIG. 34.—Myrobalans.

darker the external colour, but that this has no effect on the colour of the liquors or the leather made from it.

Myrobalans gives a rather mellow tannage, and when used alone is said to give a spongy leather. Its affinity for hide substance is exceedingly small, and it penetrates very slowly. It contains a large proportion of ellagitannic acid which ferments rapidly and deposits a light-coloured "bloom." It is not considered, however, a good weight-giving material. The tannin strength is not largely different from valonia, but the latter is much dearer. It has been found that when blended in small quantity with certain other materials the ordinary colour produced by these is greatly improved, a much brighter effect being obtained. One of the greatest uses of myrobalans is in producing acids in the liquors, in which

respect it excels most other materials on account of the large percentage of sugars which it contains. From these considerations it is clear that myrobalans can be best used in the earlier stages of tannage, giving mellow liquors, good colour, and satisfactory plumping.

The relative value of the chief commercial varieties has been investigated by Parker and Blockey,[1] who worked with carefully selected average samples. The results are given in the following table, the varieties being named after the district from which they are obtained :—

Material.	Tannin.	Non-tannins.	In-soluble.	Water.	Red.	Yellow.	Black.
Picked Bhimley .	33·0	13·1	41·7	12·0	0·8	2·5	—
No. 1 ,, .	38·4	16·1	33·5	12·0	0·3	1·8	—
No. 2 ,, .	35·2	14·2	38·6	12·0	1·0	5·1	—
Picked Rajpore .	32·2	13·0	42·8	12·0	1·1	3·0	—
No. 1 ,, .	35·4	12·1	40·5	12·0	0·9	4·0	0·1
No. 2 ,, .	27·6	12·7	47·7	12·0	2·5	7·4	—
Picked Jubblepore	28·9	12·7	46·4	12·0	0·8	2·2	—
No. 1 ,, .	36·5	14·4	37·1	12·0	0·8	3·4	—
No. 2 ,, .	27·3	14·1	46·6	12·0	1·3	5·9	—
Vingorlas . .	31·5	9·5	47·0	12·0	1·2	3·0	—
Fair Coast Madras	34·8	15·4	37·8	12·0	1·2	3·9	—

It will be noticed that "No. 1" varieties are better than "picked," and that "B.'s" show the greatest strength, followed by "J.'s" and afterwards by "R.'s." It is also clear that the colour of the fruit is no indication either of the tannin strength or of the colour of the liquors produced therefrom. The weight-giving properties were also investigated, "J.'s" being distinctly the best, followed by "B.'s" and "R.'s" which were about the same. "No. 2" varieties were better than "No. 1," and "No. 1" better than "picked." In examining the bloom-yielding properties it was found that "J.'s" and "V.'s" gave much larger deposits than the rest, and that more than half was deposited in the first week ; whereas with the rest the reverse was true. "B.'s" were shown to be the best acid-producing variety, the "J.'s" developing least.

[1] J.S.C.I., 1903, 1183.

From these considerations it is evident that "J.'s" are most suitable for the layers and "B.'s" for the early liquors.

Divi-divi is the seed pod of a South American tree (*Caesalpina coriaria*) and contains 40 to 50 per cent. of tannin which lies almost entirely in the husk of the pod. It contains a large proportion of ellagitannic acid, and is somewhat similar to myrobalans but much more prone to fermentation and to the sudden development of a red colouring matter. It has been reported as yielding great weights in sole butt tanning, but is used chiefly as a gambier substitute for dressing leather and for the rapid drum tannage of light leather. Antiseptics prevent to some extent its rapid fermentation.

FIG. 35.—Sicilian sumach (*Rhus coriaria*).

Algarobilla is the seed pod of several other species of Caesalpina, but chiefly *C. brevifolia*. It contains 45 to 50 per cent. of tannin, mostly ellagitannic acid, which is readily extracted and fermented quickly. It is said to give better weight and firmness than *diri-diri* and is less prone to discoloration; hence its use as a myrobalans substitute in the tannage of offal. After fermentation it gives a leather of very bright colour. When algarobilla is employed the leather is very prone to mould in the sheds. It is often blended with myrobalans, divi-divi and quebracho.

Sumach[1] (Sicilian) is the leaves and small twigs of *Rhus coriaria*, which is a bushy shrub cultivated in Italy for the extensive production of this tanning material. Suckers from older plants are planted in rows during spring and begin to bear the following year, though the older plants give better

[1] "Sumac" and "shumac" are also used, the latter being the invariable pronunciation.

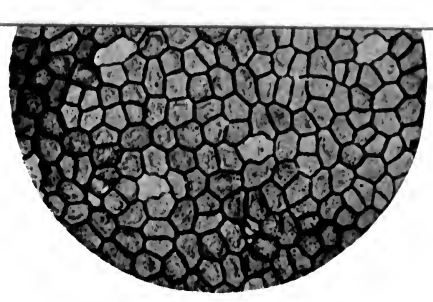
tannin strength. The leaves are picked by hand, or the shoots pruned from July to September, and dried in the sun in the fields or under cover. If the leaves only are collected the plants are pruned in winter. If pruned when gathered the dried shoots are beaten to separate leaves and stems. This is "leaf sumach," and may be exported in this state. Some, however, is packed by hydraulic press, sent to Palermo and there ground to a fine powder in stone mills. For this to be done properly there must be left in with the leaves a certain proportion of stems. The product is "ground sumach," and yields "ventilated sumach" by winnowing over a screen, the light leaves passing over and leaving the heavy stems and sand behind. "*Mascolino*" is the best sumac; *feminella* is weaker and contains a greater proportion of stems. The unpulverised portions are re-ground, and the coarse residue from this either ground again or used for fuel.

Good sumach should contain 26 to 28 per cent. of tannin, which is nearly all gallotannic acid, but it is now often adulterated with inferior materials. It is an extremely valuable tanning material, giving a soft tannage, excellent colour and a durable leather. The report of the committee[1] of the Society of Arts on book-binding leathers shows that sumach tannages are much less affected by light, heat, gas fumes, wear, and are less liable to decay, than any other tannage. It has one disadvantage, the infusion rapidly ferments, and the tannin becomes hydrolysed into gallic acid. It is extensively used for the tannage of moroccos, roans, skivers, etc., and also for bleaching the goods from darker tannages, as in the finishing of sole leather.

The common adulterants of sumach contain catechol tannins, of which pure sumach contains none, so that they may be detected by the reactions for catechol tannins (p. 115); but by far the best way is to submit the sample to a microscopic examination. The best mode of procedure is that of Lamb and Harrison as modified by Priestman,[2] in which a small amount of the suspected sample is placed in a test tube and

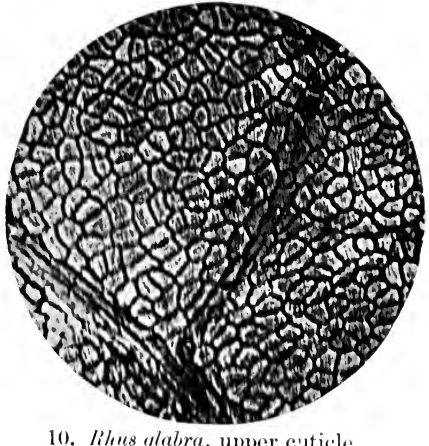
[1] J. Soc. Arts, 1901, 14.
[2] J.S.C.I., 1905, 231.

7. *Tamerix africana*, stem cuticle.



8. *Coriaria myrtifolia*, upper cuticle.

9. *Colpoon compressum*, upper cuticle.



10. *Rhus glabra*, upper cuticle.

FIG. 35A.—Photo-micrographs of sumach, its adulterants and substitutes.

subjected to the action of strong nitric acid. The temperature is gradually raised by means of a water bath.

This destroys the internal structure of the leaves, and the acid may then be neutralised with a slight excess of ammonia, the cuticles washed somewhat with distilled water and examined under a low power with transmitted light. The leaf cuticles so obtained exhibit very characteristic structures, and in this way are easily recognised. Those of sumach are characterised by numerous small hairs which are especially prominent if the cuticle be dyed with safranine.

FIG. 36.—American sumach (*Rhus glabra*).

Pistacia lentiscus ("lentisco," "schinia"), which is perhaps the commonest adulterant, contains only 12 to 15 per cent. of tannin. It gives a darker tannage than sumach, and the leather reddens on exposure to light. Its cuticles have no hairs and are more resistent to the acid and less transparent than those of sumach.

Tamerix africana ("brusca"), as small twigs, dried and ground, is imported into Sicily from Tunis for adulterating sumach. It contains 10 to 15 per cent. of tannin, produces a thin harsh leather, though of good colour. The cellular structure of the stem cuticle is rather elongated in the direction of growth, and there are no hairs.

Coriaria myrtifolia (French sumach, "stinco") contains about 15 per cent. of tannin in its leaves, which are used to adulterate sumach. It is a poisonous plant. Its cuticles have structures somewhat resembling those of pistacia, but easily distinguishable from them by a slight waviness in the cell walls.

Many other species of the Rhus family have been suggested

as tanning materials, but none are so good as *R. coriaria*. In the United States, *R. glabra* (American sumach) is somewhat extensively cultivated for this purpose, but its tannin content is distinctly less (22 to 24 per cent), and it produces also a much more yellow and dark leather, though this can be remedied somewhat—at the expense of the tannin content—by collecting the leaves earlier than is usual. *R. copallina*, which contains only about 17 per cent. of tannin, is also grown in America and used as a sumach substitute; and *R. cotinus* (Venetian sumach) is about the same strength and is also used for tanning though more important as a dyeing material.

Oakwood extract is now an exceedingly important and valuable tanning material, and is manufactured very extensively in Slavonia from the wood of the common oak (*Quercus pendunculata*),[1] which, however, only contains 2 to 4 per cent. tannin. The extract contains usually 26 to 28 per cent. tannin, and has a specific gravity of about 1·2. The tannin yields bloom and has a good combining affinity for hide substance. Its penetrating power is excellent, and its weight-giving properties and water-resisting powers are also good, so that it is widely used for making up the layer liquors of sole and dressing leathers. It is sometimes mixed with quebracho and sold as *oak-bark* extract, but the true oak-bark tannin belongs to the catechol group (see p. 133), and gives different results in practice.

Chestnut extract is extensively manufactured from the wood of the Spanish chestnut (*Castanea vesca*), which contains 3 to 6 per cent. of a tannin rather similar to oakwood. Its astringency is not so great as oakwood tannin; but its penetrating powers are even better, and its weight-giving and water-resisting powers are equally good on account of the bloom it deposits. It is used largely in a similar way to oakwood extract, and is similarly adulterated. It is a very suitable material for drum tannages.

Willow bark, from *Salix arenaria* and *S. Russeliana*, contains 7 to 11 per cent. tannin, and is used for tanning in

[1] A sub-species of *Q. robur*, see p. 133.

Russia and Denmark. It imparts to leather a characteristic odour which, when combined with that of birch tar oil, produces the well-known scent of "Russia" leather.

Knoppern are oak-galls from *Q. cerris* and other species. They form on the unripe acorn and contain up to 35 per cent. of gallotannic acid. They were at one time extensively employed in Austria for tanning, but are now largely replaced by valonia.

Turkish or **Aleppo galls** are excrescences from the young shoots of *Q. infectoria*. The tannin content is at its highest just before the gall-insect escapes, and may be nearly 60 per cent. These galls are the source of commercial "tannin," (gallotannic acid).

Fig. 37.—Common oak (*Quercus robur*).

Catechol Tanning Materials.

Oak bark, from *Q. robur* (embracing *Q. pedunculata* and *Q. sessiliflora* as sub-species), has been used as a source of tannin for many centuries. It contains up to 12 or 14 per cent. of tannin, chiefly from the catechol group, but gives a blue-black (p. 115) with iron alum, and will yield considerable bloom and gallic acid. Laevulose (fruit sugar) is also present in the bark, though uncombined with the tannin English bark (Hants and Sussex) is considered the best, though Belgian is occasionally good. Other Continental barks are distinctly inferior. Trees under 25 years old, growing in rich soils and warm situations, yield the best bark. The bark is usually peeled in April to June, when the sap is rising and the cells are multiplying, but at other seasons may be steamed off the newly-felled tree with little tannin loss. It is then piled

in the woods for a preliminary drying, and afterwards stored to complete the process. Oak-bark tannin has always been noted for the good colour, soundness, and durability of the leather it produces. Its combining and penetrating powers are also good and its weight-giving properties excellent.

Its use has nevertheless largely decreased in recent years on account of its weakness in tannin compared with other available materials, and its bulky storage. No genuine and satisfactory extract has been as yet made from it.

Gambier is a solid or pasty extract from the leaves and twigs of *Nauclea gambir*, an Eastern shrub. Like oak bark, it is one of the oldest tanning materials known in this country, and is imported to a considerable extent from Singapore, Straits Settlements, Malay Archipelago, etc. It is worked chiefly by Chinese and Malays, often with no white supervision. Shoots from older plants are planted in rows, and begin to bear in their third year. The prunings are taken to the factory, bruised, and boiled in an open boiler. The infusion is strained, concentrated until syrupy, and poured into special vessels, in which it cools and grows pasty.

In the manufacture of "cube gambier," which is the best quality, the syrup is run into trays 2 inches deep and dried in the sun. When in a sticky condition it is cut into 1½-inch cubes and dried further on cocoanut matting till the pieces occupy about 1 cubic inch. It is imported thus into this country and contains 40 to 56 per cent. of tannin. "Block gambier," an inferior quality, comes in large oblong blocks and in a more pasty condition, and when wrapped in cocoanut matting forms 1-cwt. or 2-cwt. bales. It contains 25 to 40 per cent. of tannin.

It gives a peculiar tannage, mellow and soft, and hence is used largely for sole leather in the early stages, but must be used along with other materials. There is some evidence to show that the catechutannic acid goes into the hide and is afterwards substituted by other tannins. It is an excellent thing to add to an astringent tan liquor, stopping "drawn grain." It does not give weight. It is used for the tannage of harness and dressing hides, shoe-calf and kip. It is thought that gambier tannages carry grease better than

some other tannages, and it is therefore much liked for curried work.

Quebracho is the wood of a South American tree, *Loxopteryngium Lorenzii* (Span. *Quebracho colorado*). This contains about 20 per cent. of a tannin (p. 121), which is not very soluble in water. The wood contains in addition a considerable quantity of phlobaphenes, which are also difficultly soluble, and a quebracho tannage therefore is only economical in weak liquors. The wood, which is very hard, is imported in logs and chipped into small pieces for extraction. The tannin is red, very astringent, and quickly penetrates the hide, but the material is not noted for its weight-giving properties. It produces a firm red leather, which, however, becomes distinctly darker on exposure to light. Practically no sugars are associated with it, and hence either acids or acid-forming materials must be used along with it. Its specific gravity being about 1·3, it sinks in water, and a few inches of quebracho shavings are sometimes put at the bottom of a leach (see p. 160) and used as a straining material. Mellow liquors also are sometimes sharpened by pumping them over quebracho. Though a very cheap source of tannin, it is not very popular in this country, and where used at all is generally blended with myrobalans, valonia, divi-divi or pine bark.

Quebracho extract is now commercially important and appears cheap. It is usually solid and contains about 60 per cent. of tannin and an exceedingly small proportion of non-tannins. Only weak infusions should be made up of this material also, and it should not be used for the layer liquors.

Solublised quebracho extracts are now extensively manufactured in which the difficultly soluble tannins (phlobaphenes) are brought into solution by treatment with sulphites and other alkalies, and thereby made available for tanning.[1] Such extracts are unsuitable for use in making up the layer liquors, as the deposition of the reds would be retarded by the excess of sulphites; and they have also been found to produce bad results if used in any considerable

[1] Lepetit Dollfus and Gansser, E., patent 8582, 1896.

quantity in the early stages, so that if used at all they are probably best added in very moderate quantities to the handler liquors.

Hemlock bark is obtained from the hemlock fir (*Pinus canadensis*) which is abundant in the north and west of the United States of America and in Canada. It forms the staple

FIG. 38.—Hemlock firs (*Pinus canadensis*).

tanning material of America, though other materials are now increasing in relative importance. It contains 8 to 11 per cent. of tannin and much of the phlobaphenes. It yields a red leather which darkens on exposure to light. It contains appreciable quantities of sugars, and has been successfully used alone. It is used for the tannage of sole and dressing leather, and for the manufacture of hemlock extract, in which latter case other materials are often mixed with it.

Mangrove bark, from *Rhizophora mangle*, and sometimes other species, comes from West Africa, Borneo, and other places near the coasts of tropical countries, in the tidal swamps of which it grows freely. It gives a harsh tannage of dark red colour, and is therefore not very popular, but when blended with myrobalans the colour it produces is greatly improved. Its strength is very variable, but is sometimes over 40 per cent. in tannin. Extracts are now extensively made from it, and are decolorised and sometimes sulphited. They are apt to contain common salt derived from the swamps in which the tree grew, and hence unless sparingly used they are liable to produce a rather flat leather.

FIG. 39. — Golden Wattle (*Acacia pycnantha*).

FIG. 40.—Green Wattle (*Acacia dealbata*, variety of *A. mollissima*).

Mimosa bark forms the principal tanning material of Australia and the Cape, and is obtained from various species of the Australian wattles (*acacias*). The Adelaide Golden Wattle (*Acacia pycnantha*) is the best and contains up to 50 per cent. tannin; the Sydney Green Wattle (*A. mollissima*) contains 36 to

40 per cent., and the Black Wattle (*A. binervata*) about 30 per cent. of tannin, but many other species contain considerable quantities. The Green Wattle has been transplanted to Natal, and its bark is now largely exported to England[1]. Though an astringent tannin is yielded by the bark it is not so harsh as quebracho, and does not deposit so many "reds." It penetrates fairly quickly, and gives good weights. It yields better colour than quebracho, but this is liable to darken much more rapidly on exposure to light. It is useful in this country in freshening up liquors which are too mellow, and makes a good blend with myrobalans. It also prevents too much "souring" in summer, but if used too freely in the early liquors it is liable to draw the grain.[2]

FIG. 41.—Black Wattle (*Acacia binervata*).

A. catechu, another member of the mimosa family, grows in India, and the solid extract of its wood (cutch) contains about 60 per cent. of tannin, but the material is used chiefly for dyeing. *A. arabica*, babool, also grows in India, and its bark is one of the chief Indian tanning materials. It contains 12 to 20 per cent. of tannin and much red colouring matter. Its pods, which are used for bating, contain a pyrogallol tannin of which the lime salt is soluble in water.

Mallet bark from *Eucalyptus occidentalis*, a South Australian gum, is one of the newer tanning materials and contains 45 to 55 per cent. of tannin. In some respects it resembles

[1] Hence the name "Natal Bark."
[2] See Bennett, J.S.C.I., 1908, 1193.

mimosa, but is not quite so harsh and gives light-yellow colour instead of red. It yields a fairly firm and plump leather and gives some weight.

Birch bark (inner bark of *Betula alba*, the common birch) contains about 5 per cent. of tannin. It is used with larch bark for tanning Scotch basils, and also in Russia with willow bark (p. 132). The outer bark is the source of birch tar oil, which assists in the production of the characteristic smell of Russia leather.

Larch bark, from *Pinus larix*, contains 9 to 13 per cent. of tannin of mild astringency, and also some sugary matters which assist in plumping. It is used in Scotland for tanning basils.

Pine bark, from *Pinus abies* (Norway spruce) is used extensively in Austria, and also in Russia, Germany and Denmark. It contains 10 to 14 per cent. of tannin, and a considerable proportion of sugars, and hence, in contrast with most other members of this group, will give good results alone. It gives a light-yellow leather with a characteristic pine oil smell. It is the source of the so-called "larch extract."

Canaigre is the tuberous root of a Central American red dock. The air-dried roots contain 25 to 30 per cent. of a tannin somewhat similar to that of mimosa bark. The plant grows freely in wet sandy soil and is harvested in the second year after planting. The roots are cut into thin slices and either dried at once at a low temperature or immediately converted into extract. A considerable percentage of starch is contained, and hence the extraction must be effected at temperatures between 30° and 50° C. It is used to some extent for the finishing of harness hides and light leathers.

Cape sumach consists of the leaves of *Colpoon compressum*, which contain 23 per cent. of a tannin somewhat resembling that of gambier. It is used as a substitute for Sicilian sumach.

CHAPTER XI

THE ANALYSIS OF TANNING MATERIALS

In probably no branch of analytical chemistry has there been suggested such an enormous variety of processes as in that section of technical analysis which deals with the estimation of tannin in the vegetable tanning materials. It is therefore quite impossible in this book to give any account of them, but it should be pointed out that the matter is one of exceptional difficulty, not only because the tannins are complex organic substances, but because they are also bodies of unknown constitution and molecular weight, and as a rule occur naturally in the form of mixtures one with another and with bodies which bear considerable resemblance to them in their reactions, but which are not tannins.

The Löwenthal Method at one time extensively used, is a process in which very dilute infusions of tannin are slowly titrated in the presence of an excess of indigo with a ·05 per cent. solution of potassium permanganate. The indigo itself consumes at least three-fifths of the permanganate, and a blank experiment must be made to determine the correction; but it also regulates the extent of the oxidation and acts as an indicator for the attainment of this desired limit. Any variations in the methods of manipulation of different analysts are overcome by standardising the permanganate solution against a per cent. solution of gallic acid, in which precisely the same method is used as with the solution of unknown strength. As the rate of addition and admixture of the permanganate has a very appreciable influence on the result, this point is one of considerable importance. The "unknown" solution is afterwards treated with a gelatin solution in the presence of salt and sulphuric acid, and the separation of the precipitate of "amorphous leather" is assisted by the addition of a little kaolin. It is probably better to use hide powder, prepared as described

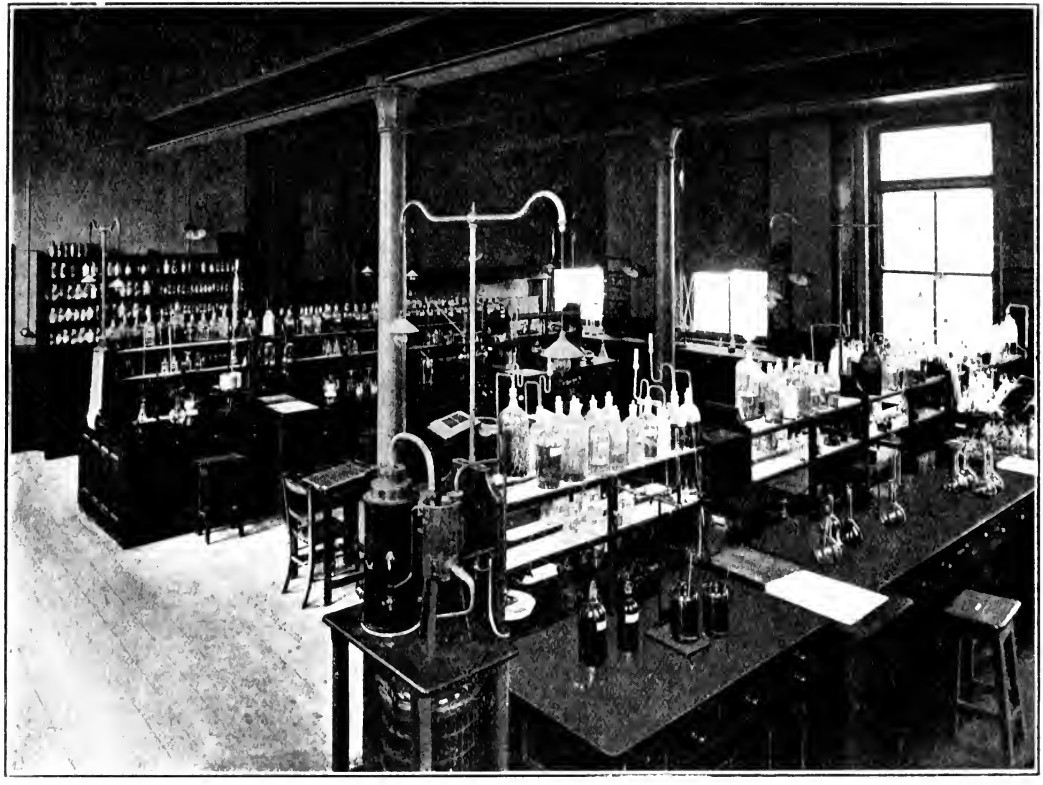


Fig. 42.—Students' laboratory, Leather Industries Department of the University of Leeds.

below, for detannising. An aliquot part of the filtrate is then titrated as before, and the amount of permanganate consumed by oxidisable non-tanning bodies is thereby determined and correction made accordingly. This method can be made to give fairly concordant results, and where a large proportion of free acids and of gallic acid and other oxidisable non-tanning matters are present, *e.g.*, in tan-yard liquors it will probably yield also the most accurate results.[1]

The Indirect Gravimetric Method, however, has been for many years the most important method, and has been employed by the members of the International Association of Leather Trades Chemists (I. A. L. T. C.) since its formation in 1897. Its principal operations are those of filtration and detannisation, measured volumes of the unfiltered, filtered, and detannised infusion being evaporated to dryness in tared basins and the residues weighed. The amount of matter removed by filtration and detannisation is thus indirectly weighed, and the proportion of "insoluble matter" and "tanning matter" thereby determined, whilst those substances still unremoved from solution are calculated as "soluble non-tanning matters."[2] The detannisation, involving the removal of tannin from the solution, is accomplished by means of "hide powder," which is merely powdered hide substance specially prepared for this process. The method will now be described in greater detail.

Sampling the material for analysis is the first important consideration, and must be very carefully done if a correct judgment is to be formed of the material, and if concordance between more than one chemist is desired. In weighing out the sample for analysis equal care should be taken to obtain a representative portion as in sampling from bulk. The directions of the I. A. L. T. C. are as follows :[3]

SAMPLING FROM BULK.

1. *Liquid extracts.*—In drawing samples, at least 5 per cent. of the casks must be taken, the numbers being selected as far apart as possible.

[1] See Procter and Hirst, J.S.C.I., 1909, 293 and 294.

[2] These determinations are often spoken of as "insolubles," "tannin," and "non-tannins."

[3] See London Report, pp. 22—29, and 124.

The heads must be removed, and the contents mixed thoroughly by means of a suitable plunger, care being taken that any sediment adhering to sides or bottom shall be thoroughly stirred. All samples must be drawn in the presence of a responsible person.

2. *Gambier and pasty extracts.*—Gambier and pasty extracts should be sampled from not less than 5 per cent. of blocks, by a tubular sampling tool, which shall be passed completely through the block in seven places. Solid extracts shall be broken and a sufficient number of portions drawn from the inner and outer parts of the blocks to fairly represent the bulk.

3. *General tanning materials.*—Valonia, algarobilla, and all other tanning materials containing dust or fibre, shall be sampled, if possible, by spreading at least 5 per cent. of the bags in layers one above another on a smooth floor, and taking several samples vertically down to the floor. Where this cannot be done, the samples must be drawn from the centre of a sufficient number of bags. While valonia and most materials may be sent to the chemist ground, it is preferable that divi-divi, algarobilla, and other fibrous material shall be unground. Bark in long rind and other materials in bundles shall be sampled by cutting a small section from the middle of 3 per cent. of the bundles with a saw.

4. *Other directions.*—All samples shall be rapidly mixed and enclosed at once in an air-tight bottle or box, sealed and labelled. Samples to be submitted to more than one chemist must be drawn as one sample, well mixed, then divided into the requisite number of portions, and at once enclosed in suitable packages.

Preparation for Analysis.

1. *Liquid extracts.*—Liquid extracts shall be thoroughly stirred and mixed before weighing, which shall be rapidly done to avoid loss of moisture. Thick extracts, which cannot be otherwise mixed, may be heated to 50° C., then stirred and rapidly cooled before weighing; but the fact that this has been done must be stated in the report.

2. *Solid extracts.*—Solid extracts shall be coarsely powdered and well mixed. Pasty extracts shall be rapidly mixed in a mortar, and the requisite quantity weighed out with as little exposure as possible to avoid loss of moisture. Where extracts are partly dry and partly pasty, so that neither of these methods is applicable, the entire sample shall be weighed and allowed to dry at the ordinary temperature sufficiently to be pulverised, and shall then be weighed, and the loss in weight taken into calculation as moisture. In such cases as gambier, in which it is not possible to grind or by other mechanical means to thoroughly mix the constituents of the sample, it is permissible to dissolve the whole, or a large portion of the sample, in a small quantity of hot water, and immediately after thorough mixing to weigh out a portion of the strong solution for analysis.

3. *General tanning materials.*—The whole sample, or not less than 250 gms., shall be ground in a mill until it will pass through a sieve of 5 wires per centimetre. Where materials, such as barks and divi-divi, contain fibrous materials which cannot be ground to powder, the ground sample shall be sieved, and the respective parts which do and do not pass through the sieve shall be weighed separately, and the sample for analysis shall be weighed so as to contain like proportions.

Preparation of the infusion.—In the case of solid materials like sumach, valonia, etc., extraction is necessary and is

usually accomplished by means of Procter's apparatus (Fig. 43). The principle of this is that the requisite quantity of material is digested for some hours in cold distilled water, and subsequently percolated with further quantities of water, the temperature of which is gradually increased to boiling point. The extraction apparatus consists of an ordinary open beaker, which is placed in a water bath. A common thistle-head funnel is bent twice at right angles to form a syphon. The head, covered with silk gauze, rests on the bottom of the beaker, the other end being lengthened by a piece of slender glass tube, connected by indiarubber tube fitted with a screw pinch-cock, the whole being held in position by a clamp. The beaker is filled with sand and tanning material, water is poured in, and the whole raised to the requisite temperature in the water bath, when percolation is started by sucking, and warmed water added as required.[1] The percolate is collected in a litre flask. In this way a rapid and complete extraction of the material is obtained with less than one litre of water, and if the greater part of the infusion be obtained below 50° C. (see Regulations, p. 150), the destruction of tanning matter is quite negligible. The precautions to be taken in dissolving extracts, etc., are given in the official regulations (p. 151). In all cases the volume, after cooling, is made up to 1 litre and the infusion thoroughly mixed. As practically all materials contain substances which are partially soluble, and other bodies whose degree of absorption by hide powder is dependent upon the concentration of the solution, the whole method of analysis is quite empirical, and it has been found necessary for concordance to limit the tannin content of the infusion within ·35 and ·45 per cent. To obtain such

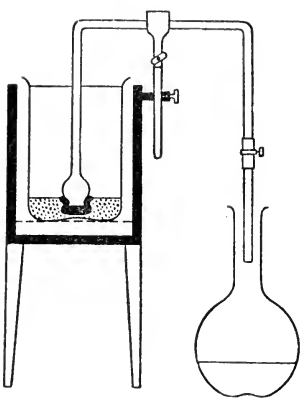


Fig. 43.—Procter extractor.

[1] L.I.L.B., 2nd ed., p. 185.

infusions the strength of the material to be analysed must be roughly known in order to determine the quantity which should be weighed out, for if the strength of solution should be afterwards found to be outside the specific limits the whole analysis must be repeated. The approximate amounts of different materials to be taken for 1 litre of infusion are as follows :—

Unextracted materials.		Extracts.	
Sumach	15 gms.	Oakwood	16 gms.
Pistacia	20—30 gms.	Chestnut (liquid)	14 gms.
Valonia	14—15 gms.	,, (solid)	7 gms.
Valonia beard	10—11 gms.	Quebracho (liquid)	9—13 gms.
Myrobalans	15 gms.	,, (solid)	6 gms.
Divi-divi	9 gms.	Mimosa D.	10—12 gms.
Algarobilla	8—9 gms.	Myrobalans (liquid)	16 gms.
Oak bark	30—36 gms.	Gambier (cube)	7—9 gms.
Oak wood	50—100 gms.	,, (block)	10—12 gms.
Hemlock bark	32—36 gms.	Mangrove (liquid)	9 gms.
Mimosa bark	11 gms.	,, (solid)	7 gms.
Quebracho wood	20—22 gms.	Cutch	7 gms.
Mangrove bark	10 gms.	Pine bark	16 gms.
Pine bark	32 gms.	Hemlock	10—14 gms.
Willow bark	36 gms.		
Chestnut wood	45 gms.		
Canaigre	15—18 gms.		
Spent tans	50—100 gms.		

Filtration.—This is sometimes a matter of considerable difficulty, for many infusions of tanning materials (*e.g.*, that of quebracho wood or extract) contain very finely-divided particles of the phlobaphenes, etc., and for such solutions all ordinary filter papers are quite inefficient. Schleicher and Schull's "No. 590" paper will be found to answer for a great many tanning materials, and S. & S. "No. 605 extra hart" will work even with the most obstinate cases. The filtration is often assisted to a considerable degree by the addition of 1 or 2 gms. of kaolin to the infusion, but both kaolin and filter papers absorb very appreciable amounts of tannin and other colloidal matters from the solution; so that whatever paper is employed, and whatever amount of kaolin is used along with it, a correction must be always determined

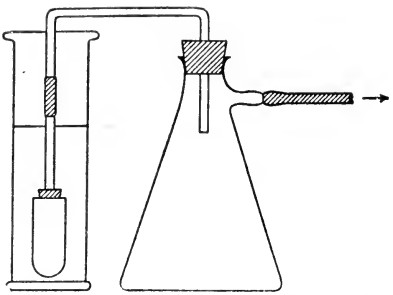


FIG. 44. — Filtration apparatus with Berkefeld candle (upward filtration).

for that particular process and applied to every analysis in which that process is used. A further disadvantage of all filter-paper methods is that they are always exceedingly slow, and a very useful alternative method is that introduced by Parker and Payne in 1904,[1] involving the use of the Berkefeld "filter candle," a cylinder of kieselgahr about 7 cms. long. This is open at one end, having an external diameter of 3 cms. and an internal diameter of 1 cm. Into the open end is fitted a rubber bung through which passes a glass tube connected with an ordinary vacuum flask. The air is exhausted from this by a water pump or syringe and the liquor sucked through the thick layer of siliceous earth, which thereby acts as the filtering medium (see Figs. 44 and 45).

If a quantity of the filtrate which is first obtained be rejected no correction is necessary and a comparatively rapid filtration of the liquor is obtained. With some materials, however, the filtrates are turbid and need to be repeatedly re-filtered in order to obtain them "optically clear both by reflected and transmitted light" (see Regulations, p. 150).

Detannisation.—The manner in which hide powder has been

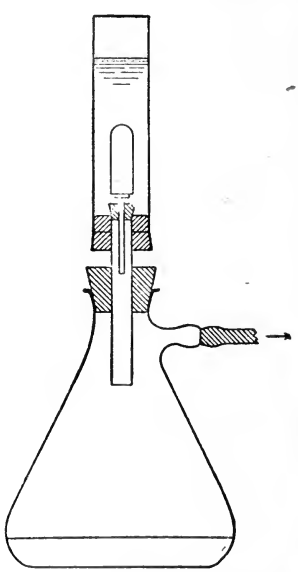


FIG. 45.—Filtration apparatus with Berkefeld candle (downward filtration).

[1] Collegium, 1904, 249.

used for removing the tannin from solution varies very considerably, but from 1897 to 1907, the official method of the I. A. L. T. C. was that of Procter, in which a "filter bell" (Fig. 46) was carefully filled with the hide powder and the liquor allowed to soak up into this by capillary attraction, and afterwards slowly syphoned over into a receiving vessel, the first 30—35 cc. being rejected and 50 cc. pipetted off from the next 60 cc. for evaporation to dryness. This method was a great improvement on earlier maceration processes in rapidity, accuracy and concordance, and for nearly twenty years was quite generally used throughout Europe. Later experiment, however, showed that it was open to various sources of error, among which were the imperfect removal of soluble matter in the powder by the mere rejection of the first 30 cc. of percolate, the successive change in the composition of the filtrate according to the amount which had previously come over, the difficulties experienced in the satisfactory "packing" of the filter bell with the powder, which operation required considerable care and some skill, and the impossibility of carrying out the process when any quantity of free acid was present in the infusion to be detannised. One of the greatest objections to the filter bell was that the solution is almost completely detannised by the first portions of the hide powder it meets, and hence that this detannised solution has to flow through a certain amount of fresh and very absorptive hide powder which readily takes out of solution many soluble non-tanning matters and so causes them to be reckoned as tannins.

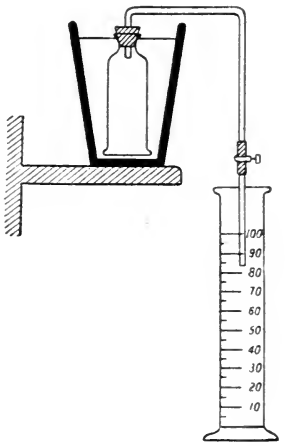


FIG. 46.—Procter's filter-bell apparatus.

Some of these sources of error were partially overcome by the use of chromed powder, but still more so by the method adopted by the leather chemists of America in which the

powder is first lightly chromed with chrome alum, afterwards washed free from soluble matter, and then immediately introduced into the tannin infusion and vigorously shaken for ten minutes. All these methods were very carefully compared on the same solutions in an extensive investigation by Dr. Parker and the Author,[1] in which artificial mixtures of known composition were used, as well as commercial samples, so that the extent of the error with each method could be accurately determined. The results showed that although the concordance obtained by the use of lightly-chromed powder in the

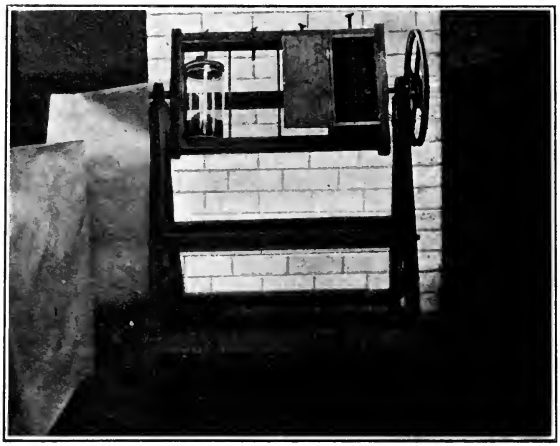


FIG. 47.—Shake machine for the Procter-Bennett method of tannin analysis.

filter bell was on the whole better than with unchromed powder, the extent to which soluble non-tanning matters were absorbed was distinctly greater, whereas with the "shake method" the concordance was decidedly better and the absorption of non-tannins less. An investigation of the "shake method" as used in America was made by Prof. Procter and the Author,[2] its defects being pointed out and suggestions made for a modified and improved process. These suggestions were afterwards crystallised into definite proposals[3] in

[1] Parker and Bennett, J.S.C.I., 1906, 1193.
[2] Procter and Bennett, J.S.C.I., 1906, 1203.
[3] Procter and Bennett, J.S.C.I., 1907, 79.

the "basic chloride method," which was soon adopted by the I. A. L. T. C. (see Regulations, below), as their official method of analysis. The "shake machine" used by Procter and Bennett is shown in Fig. 47.

In this method the powder is chromed rather more heavily than in the American method and in a very much shorter time, and the process of washing the powder is also subjected to a definite chemical control. The correction necessary for the dilution of the infusion by the moisture in the prepared powder is also made easy to apply and is the same for every analysis. The amount of hide powder for each analysis is also made definite and the conditions of experiment so arranged that the chances of concordance are at a maximum. In a later paper[1] the Author pointed out the importance of the *texture* and *acidity* of the original unchromed hide powder and gave results showing the influence of these factors. He therefore suggested that hide powder should be "standardised" like any other chemical reagent, and specified the limits within which this might be done. These proposals were also embodied in the official method of the I. A. L. T. C.

Evaporation and Drying.—This is best accomplished by pipetting 50 cc. of the unfiltered, and filtered infusions and 60 cc. of the detannised solution into tared porcelain basins and evaporating to dryness on a steam bath. The basins with their residues are then dried to constant weight in the vacuum oven. Where no vacuum oven is available, a steam or water oven is quite efficient, though somewhat slower. An air oven at 105° C. was often used, but is very liable to cause oxidation of the residues, and is now not used in official analyses. Where materials are being analysed in which extraction has been necessary, there is nothing gained by evaporating any of the unfiltered percolate to dryness, for most of the insoluble matter still remains in the extractor with the sand. In this case, therefore, it is necessary to take a separate portion of the original sample and determine the total amount of dry solid matter (and, of course, water also) in it by drying in the oven until constant. As the amount of "soluble solids" is determined

[1] Bennett, J.S.C.I., 1907, 455.

from the filtered solution, the amount of "insolubles" is then obtained by difference. With extracts the amount of water is determined indirectly by the weight of the residue from the unfiltered infusion ("total solids"), and hence in every case the analytical result is stated as in the following example:—

OAKWOOD EXTRACT.

Tannin	25·4
Soluble Non-Tannins . . .	18·1
Insoluble in water at 17·5° C. . .	0·0
Water	56·5
	100·0 per cent.

Spent tanning materials are usually stated in terms of the *dry* material, but may be calculated in terms of the unleached material by means of the "insolubles," which are assumed to be unaffected by the leaching.

The actual regulations of the I. A. L. T. C. for their official method of analysis are as follows:—

GENERAL REGULATIONS.

The Executive Committee have decided that any method which conforms to the conditions of sections 1 to 4 of the following statement may be regarded as conforming to the recommendations of the International Commission on tannin analysis, but, that members of the International Association must work according to the detailed directions contained in sections 5 to 8.

1. *The solution for analysis* must contain between 3·5 and 4·5 gms. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C., but if the Teas Extractor be used, the first portion of the extract shall be removed from the influence of heat as soon as possible.

2. "*Total solubles*" must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cms. thickness, and a layer of 1 cm. deep in a beaker placed in a good light on black glass or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied as described in section 6. Filtration must take place at a temperature between 15° C. and 20° C. Evaporation to dryness shall take place between 98·5° C. and 100° C. in shallow flat-bottomed basins which shall afterwards be dried until constant at the same temperature, and cooled

before weighing for not less than twenty minutes in air-tight dessicators over dry calcium chloride.

3. "*Total solids*" must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution at a temperature between 98·5° C. and 100° C. in shallow flat-bottomed basins which shall afterwards be dried until constant at the same temperature and cooled before weighing for not less than twenty minutes in air-tight dessicators over dry calcium chloride. "Moisture" is the difference between 100 and the percentage of total solids, and "insoluble" the difference between "total solids" and "total solubles."

4. "*Non-tannins.*"—The solution must be detannised by shaking with chromed hide powder till no turbidity or opalescence can be produced in the clear solution by salted gelatine. The chromed powder must be added in one quantity equal to 6·0 to 6·5 gms. of dry hide per 100 cc. of the tanning solution, and must contain not less than 0·2 and not more than 1 per cent. of chromium reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water, not more than 5 mgr. of solid residue shall be left on evaporation of 100 cc. All water contained in the powder should be determined and allowed for as water of dilution.

I. A. L. T. C. Official Method.

The following sections give the detailed method of carrying out the analysis adopted by the I. A. L. T. C. for the use of its own members.

5. *Preparation of infusion.*—Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 gms. of tanning matter per litre, and not less than 3·5 or more than 4·5 gms. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature 17·5° C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials, previously ground till they will pass through a sieve of 5 wires per centimetre, are extracted in Koch's or Procter's extractor with 500 cc. of water at a temperature not exceeding 50° C. and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must after cooling be accurately made up to 1 litre.

6. *Filtration.*—The infusion shall be filtered till optically clear (see section 2). No correction for absorption is needed for the Berkefeld candle, or for S. & S. 590 paper if a sufficient quantity (250—300 cc.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of

filtration are employed the average correction necessary must be determined in the following manner. About 500 cc. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 cc. is evaporated to determine "total soluble No. 1." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible) and 50 cc. is evaporated to determine "total soluble No. 2." The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 cc. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 cc. of clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(Note. It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is appromixately constant for all materials, and amounts in the case of S. & S. 605, 150 cc. being rejected, to about 5 mgr. per 50 cc. and where 2 gms. of kaolin are employed in addition, to 7½ mgr. The kaolin must be previously washed with 75 cc. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.)

7. *Detannisation.*—Hide powder shall be of woolly texture, thoroughly delimed, preferably with hydrochloric acid, shall not require more than 5 cc. or less than 2·5 cc. of N/10 NaOH or KOH to produce a permanent pink with phenol phthalein on 6½ gms. of the dry powder suspended in water. If the acidity does not fall within these limits, it must be corrected by soaking the powder before chroming for twenty minutes in 10—12 times its weight of water to which the requisite calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70—75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgms. per 100 cc. The powder when sent out from the makers shall not contain more than 12 per cent. of moisture, and shall be sent out in air-tight tins.

The moisture in the air-dried powder is determined and the quantity equal to 6·5 gms. actual dry hide powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately ten times its weight of distilled water[1] (2 gms. per hundred of dry powder of crystallised chromic chloride ($Cr_2Cl_6 \cdot 2H_2O$)[2]) is now dissolved in water and made basic with 0·6 gms. Na_2CO_3 by the gradual addition of 11·25 cc. of N/1 solution, thus making the salt correspond to the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder and the whole churned slowly for one hour. In laboratories when analyses are continually being made it is more convenient to use a 10 per cent. stock solution, made by dissolving 100 gms. of $Cr_2Cl_6 12H_2O$

[1] Very woolly powders require slightly more than 10 times their weight of water.

[2] Kahlbaum.

in a little distilled water in a litre flask, and very slowly adding a solution containing 30 gms. of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution 20 cc. per 100 gms. or 1·3 cc. per 6·5 gms. of dry powder should be used.

At the end of one hour the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until on adding to 50 cc. of the filtrate, 1 drop of 10 per cent. K_2CrO_4 and four drops N/10 $AgNO_3$, a brick-red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0·001 gm. of NaCl in 50 cc.

The powder is then squeezed to contain 70—75 per cent. water, and the whole weighed. The quantity Q containing 6·5 gms. dry hide is thus found, weighed out, and added immediately to 100 cc. of the unfiltered tannin infusion along with (26·5—Q) of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, 1 gm. of kaolin added to the filtrate, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 cc. of the filtrate is evaporated and reckoned as 50 cc., or the residue of 50 cc. is multiplied by $\frac{6}{5}$. The non-tannin filtrate must give no turbidity with a drop of a 1 per cent. gelatine 10 per cent. salt solution. The kaolin may be used by mixing it with the hide powder in the shaking bottle.

8. *The analysis of used liquors and spent tans* shall be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being diluted, or concentrated by boiling *in vacuo* or in a vessel so closed as to restrict access of air, until the tanning matter is if possible between 3·5 and 4·5 gms. per litre, but in no case beyond a concentration of 10 gms. per litre of total solids, and the weight of hide powder used shall not be varied from 6½ gms.

The results shall be reported as shown by the direct estimation, but it is desirable that in addition efforts shall be made, by determination of acids in the original solution and in the non-tannin residues, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide powder, and hence returned as "tanning matters." In the case of tans it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight or to grams per 100 cc.; and in both cases the specific gravity shall be reported.

Reports of analyses shall only be sent out on a mean of at least two separate analyses which closely correspond.

9. All evaporation shall be rapidly conducted at steam temperature in shallow flat-bottomed basins of not less than 6·5 cms. diameter to apparent dryness; and shall be subsequently dried between 98° and 100° C. in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight dessicators over dry calcium chloride for at least twenty minutes, and then weighed rapidly. Not more than two basins shall be placed in one dessicator, and the basins must not be wiped after removal from the dessicator.

The measurement of colour in tanning materials is also a matter of considerable importance, and is usually accomplished

by means of "Lovibond's tintometer." In this instrument a layer of the filtered solution (as used in analysis) is matched in colour by slips of coloured glasses (red, yellow and blue), which are carefully graduated in units and decimals of colour and arranged so that equal numerical quantities in these colours will always produce a neutral tint. The liquor is contained in a cell 1 cm. thick, and the results are calculated to $\frac{1}{2}$ per cent. solution of tanning matter.

Another method is actually to tan a piece of calf or sheep grain carefully delimed with 2 per cent. boric acid, 1 per cent. phenol solution. Such a process will give comparable results if its manipulative details are kept always the same.

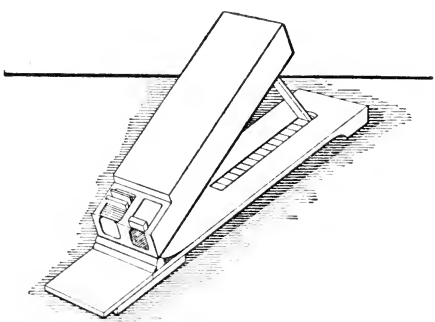


Fig. 48.—Tintometer.

In the analysis of tan-yard liquors an important determination is that of the amount of free acid present. This, however, is exceedingly difficult to bring about, although many methods have been suggested. The author has tested the most important of these[1] and found that the most generally useful is that due to Procter, in which 10 cc. of filtered tan liquor is measured into a beaker and titrated with a saturated solution of lime water until a trace of permanent precipitate is obtained. The free acids are then neutralised and the calcium tannates begin to be precipitated. For all ordinary yard control the number of cc. saturated lime water so consumed may be taken as the result, but the lime water can be accurately standardised by means of N/10 hydrochloric acid and phenol phthalein, and the result calculated in terms of any particular acid.

An exceedingly useful instrument in the tan yard for determining roughly the strength of the liquors is the "barkometer,"

[1] Bennett and Wilkinson, J.S.C.I., 1907, 1186.

which is a glass or brass hydrometer whose readings may be converted into specific gravity by dividing by 1,000 and adding 1, and therefore indicate the second and third decimal places of ordinary specific gravities, *i.e.*, a liquor of barkometer

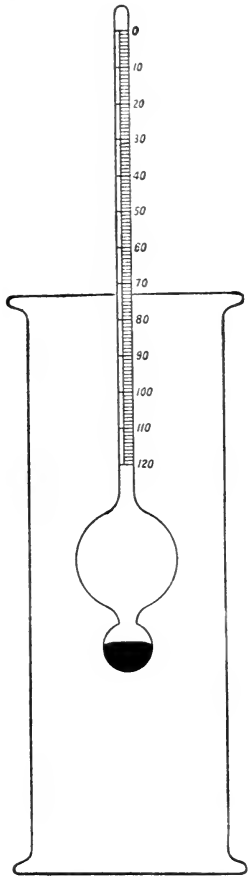


FIG. 49.—Barkometer.

strength 43° has a specific gravity of 1·043. The barkometer strength (or S.G.) of a tan-yard liquor is, however, no guide at all to the actual tanning strength of the liquor, as this is also dependent upon the amount of non-tannins in the liquors, and these vary very considerably with different tanning

materials. A quebracho liquor 20° Bkr. and an oakwood liquor 40° Bkr. might have the same tannin strength. The barkometer is nevertheless widely used in tanneries, for although its readings bear no direct relation to the tannin content, it will at any rate give in the tannage of any particular class of goods a fairly accurate indication of the loss in tannin strength of the liquors as the goods are passed through them, and it is for this purpose that it is so extensively used. The reading should be taken where the curved surface of the water touches the barkometer stem.

Extracts are often sold as having a certain strength in Beaumé degrees. This is quite an arbitrary scale of specific gravity, but its readings may be roughly judged from the following table of the "Rational Scale."

BÉAUMÉ HYDROMETER SCALE.

Béaumé Degrees.	Specific Gravity.	Béaumé Degrees.	Specific Gravity.
0	1·0000	40	1 3834
5	1·0358	45	1 4531
10	1·0745	50	1·5301
15	1·1160	55	1·6158
20	1·1608	60	1·7116
25	1·2095	65	1·8195
30	1·2624	70	1·9090
35	1·3202	75	1·9600

Degrees Twaddell are hydrometer readings in which each degree corresponds to 5° Bkr.

CHAPTER XII

THE PREPARATION OF THE TANNING LIQUORS

Grinding.—Nearly all solid materials, whether they are intended for leaching or for dusting material, require reducing to a finer state of division in order to allow a more complete and easy extraction of the tannin. In doing this a certain amount of crushing as well as cutting is desirable to destroy the cellular structure in which the tannin is contained.

With oak bark, some preliminary preparation for true grinding is often desirable, and the material is "hatched" into

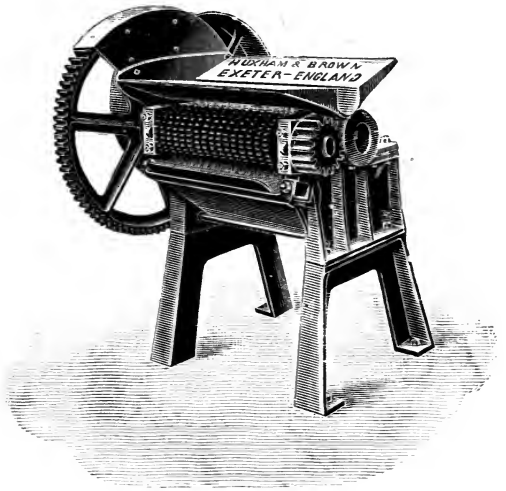


FIG. 50.—Bark breaker.

pieces a few inches long by chopping by hand, or by cutting with a machine having a fly wheel with radial knives, somewhat like a chaff cutter. In place of hatching "bark breakers" (Fig. 50) are often used, in which two toothed rollers, made to fit each other, crush and break the material. The bark is then

ground in some variety of that large class of mills which consist essentially of two toothed cones (see Fig. 51), one of which is usually fixed whilst the other rotates about its axis. One of these cones is within the other, but the axes may be vertical or horizontal, according to the other arrangements of the machine. The bark breaker may be attached to the mill and arranged to feed it.

Valonia for dusting purposes should be ground in a similar mill, but for leaching the result is too fine a dust to allow a thorough percolation of the leach liquor, and may also cause a caking of the material, in which case the internal part is scarcely leached at all. Hence a better way is to crush the cups by passing through two fluted rollers, the cellular structure being thereby sufficiently destroyed to allow a thorough extraction, and the product not too finely divided to permit a free permeation of the liquor in the leaches.

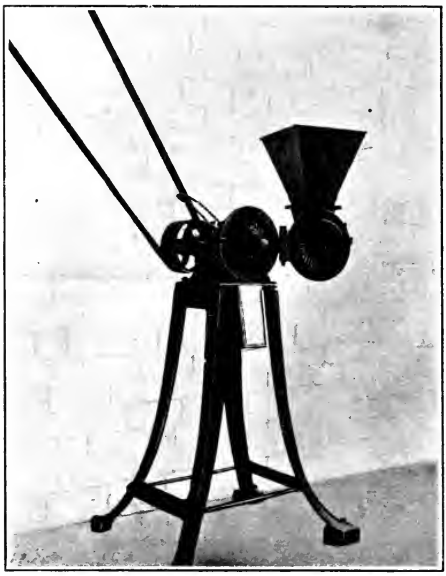


FIG. 51.—Grinding mill.

Myrobalans for leaching should also be put through this machine (often called a myrobalans crusher), but when required for dusting purposes should not be ground, for although it is wanted in a fine state of division, the stones of the nuts are very hard and may injure the mill's teeth, and the softer part of the nut is very apt to cause clogging in the ordinary mill, so that the usual plan is to use some form of "disintegrator." The principle of these machines is that very rapidly revolving beaters, either radial or concentric steel bar

cylinders, dash the material against a serrated surface and knock it to a powder. Into the serrated case is fixed a grating which allows the exit of the dust. Hard and tough barks, which are not brittle (*e.g.*, mimosa bark), can also be satisfactorily pulverised in these machines. Their disadvantage is the great proportion of exceedingly fine dust which they make, necessitating its collection in silk bags, and their liability to cause fire.

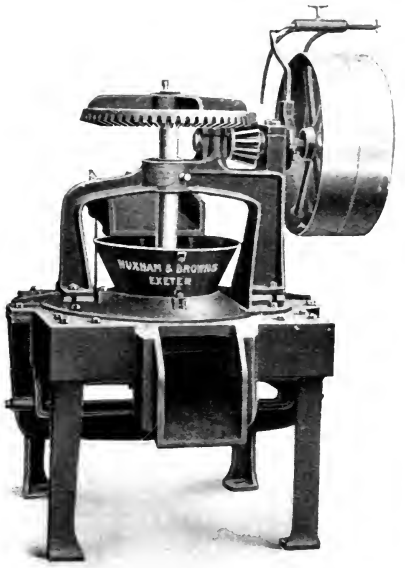


FIG. 52.—Myrobalans husking machine.

Hard and brittle materials can be reduced by the use of toothed saws or rasps, and many American mills have been made on this principle, and have proved particularly suitable for hemlock bark. With such materials, also, "shaving" or "shredding" mills are quite efficient. They consist essentially of knived cones, wheels, or cylinders which are rotated at a high speed and have the material (quebracho wood, hemlock bark, oakwood, etc.), fed against them by toothed rollers. Divi-divi and algarobilla do not need either grinding or

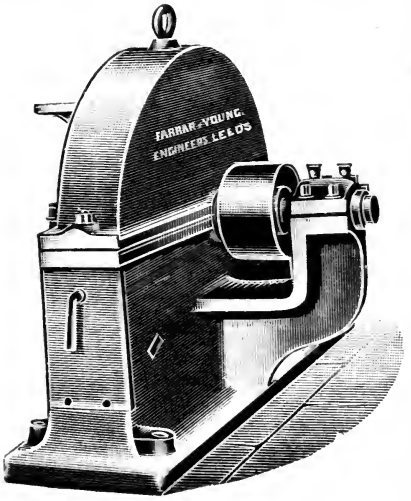


FIG. 53.—Disintegrator.

extracting, as their tannin is very loosely held and readily fermentable.

Leaching was first used to complete the extraction of solid materials used in the later stages of tanning, and afterwards to make strong liquors for these stages, but the introduction of extracts has now made the preparation of strong liquors a matter of comparative ease, whilst at the same time the greater variety of tanning materials now employed and the better knowledge of the chemistry of some of the more unstable tannins, has assisted largely in the return to the old system of leaching only the partially spent material used in the "layers" (p. 177), technically termed "fishings." Valonia, for example, which is extensively used for making up sole leather layer liquors, should never be leached for this purpose, because as mentioned earlier (p. 126), its bloom deposits rapidly and would merely form an insoluble precipitate in the leaches, and be lost to the tanner. What is desired is that the ellagitannic acid should be extracted, go into the hide and there deposit its bloom, giving the desired results of firmness, water proofness, and weight. For some dressing leather tannages, however, the more astringent ellagitannic acid is not wanted, and the valonia should then be leached to allow its decomposition before the liquors are made up. These considerations have also to be borne in mind in deciding whether it is desirable to pump used liquors back again over the leaches, or to work them down the yard. In an ordinary mixed tannage of sole and heavy leathers the latter course is clearly the best, in order to use the fermentable tannin whilst it is in solution, but where only stable tannins are employed, such as in a pure oak bark yard, the old and weakened liquors might then be strengthened by passing them again through the leaches. Similar considerations have to be taken into account in the case of those materials which rapidly deposit reds.

Leaching is in this country usually done in square pits sunk in the ground and built of brick and cement, or Yorkshire flagstone; though also sometimes of wood. A series of such pits is employed and worked on some systematic process of a continuous extraction of the materials with water, in which it is arranged that the fresh material is acted upon by the

strongest liquor of the series, and the nearly "spent" material with fresh water or the weakest liquor. In this way, the liquor is gradually strengthened until it becomes the strongest liquor of the series, and is used as the source of the strong tanning liquors which are then worked down the yard to form the "sour" and "mellow" liquors (pp. 169—171), used in the early stages of tanning. Each leach pit is provided with a

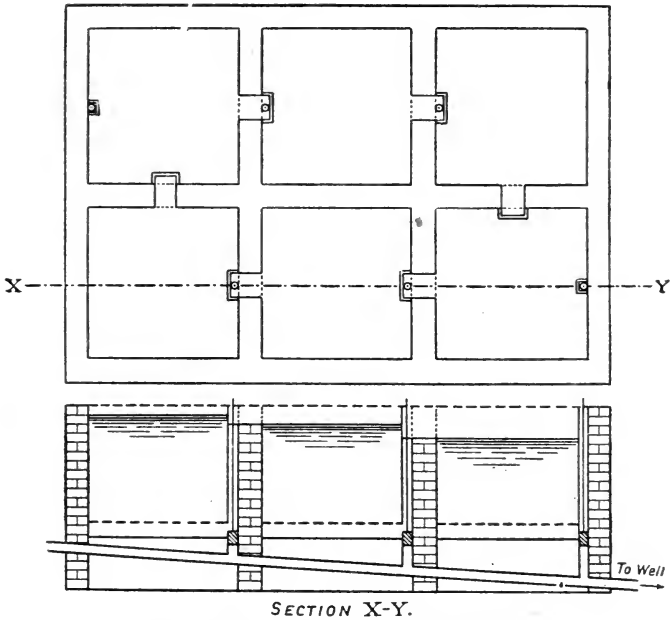


FIG. 54.—Battery of press leaches.

false bottom, and with a wooden shaft or "eye," which passes down the side of the pit in one corner and communicates with the space below the false bottom, and also with a plug which allows the leach liquors to be run at any time into a deep well.

In one method of leaching, the strong liquor is run off and the next strongest liquor pumped over the material left behind, the third strongest pumped over the next pit, and so on, water being pumped on the last and nearly spent pit. This system

requires a good deal of pumping, and when the liquors are run off, the materials settle, and often will not rise again satisfactorily. These difficulties are only imperfectly overcome by forcing the liquor in at the bottom.

Hence a deservedly popular method of leaching is now the **press leach system,** in which the liquor is pressed round the "battery" of pits by virtue of its own weight and constantly increasing specific gravity, a certain amount of fall being allowed. The liquor passes downward through the leach and up a vertical spout connected with the next stronger leach by a short trough or pipe, which must be of ample size to allow easy percolation, and which can be closed when necessary. When the battery is in actual work, the strong liquor of the "head leach" is run off to make up the tanning liquors, and water is pumped on to the "tail leach" containing the nearly spent material, which causes the liquor to press round into the next pits until the head leach is again full. The material of the tail leach is now exhausted, so that the liquor is run to the well, and the spent tan cast, pressed, and burnt as fuel. Into the now empty leach pit is placed the fresh batch of material for extraction, and this pit is now made into the head leach by pumping the weak liquor in the well on to the next pit, which contains the weakest material, and causing the liquor to press round into the newly made up leach, which then becomes the source of the tanning liquors. The arrangement of the pits is illustrated in Fig. 54, and it will be readily understood that a circular arrangement is most convenient.

If more than eight pits are employed in the same series, it is necessary to assist the pressing round by a certain amount of pumping, either at some definite intermediate stage or by a series of pumps on the Holbrook system in which each vertical spout is provided by a simple pump driven by power. Another arrangement sometimes convenient is to have two distinct press leach batteries, the strongest liquor of one being the source of the weak liquor for the other, but this system involves both more pumping and the removal of the material being extracted from one battery to the other. Circular vat leaches are sometimes used instead of pits, especially in the United States, but are not so durable.

The efficiency of the leaching arrangements determines the amount of tannin going to waste in the so-called spent tan, and hence the matter is one of considerable economical importance. With care the tannin content can be reduced below 1 per cent., and with some materials (*e.g.*, oak bark) it is desirable for economy to do this, but where the materials are mixed, and many contain unstable tannins, it becomes a question whether it may not be better to have a smaller system of leaches, which gets the liquors quickly forward and into the yard, thus saving a considerable amount of decomposable tannin and allowing the loss of a less amount of difficultly extractable tannin, by letting the spent tan go with 2 or 3 per cent. more tannin than is usually considered desirable. The extent to which this is done depends almost entirely upon the arrangements and facilities of each particular yard and the class of leather being made. The same policy may be adopted in those cases where a material improvement in colour may be gained by not pushing the extraction too far, and in the leaching of fairly strong materials.

The question of heating the leach liquors is also important. Just as in analytical work, where cold water was used to extract the first part of the tannin, and hot water to remove the last traces, so also is it desirable in practice, for heated infusions are apt to give dark colour, yield insoluble matter, and decrease in tannin strength. When only used in the extraction of the last portions, however, this effect of heat is of such small proportion that it is usually quite negligible. The heating may be done by means of steam-heated copper coils below the false bottoms—an expensive way—or by the direct but careful leading in of steam by means of special jets, but for all ordinary purposes hot water is quite sufficient. It is not essential to have the highest possible temperature, and indeed it has been shown[1] that many materials (*e.g.*, valonia, mimosa bark, sumach, and canaigre) are mostly easily extracted with only warm water (50° to 60° C.), whilst, on the other hand, it is pretty general that the colouring matters are more largely extracted at higher temperatures. Hence this

[1] Procter and Parker, J.S.C.I., 1895, 635.

matter is determined by the nature of the materials being infused. Oak bark, gambier, myrobalans, quebracho, and mangrove will do better with higher temperatures (80° to 90° C.), but with the last two the question of colour should be considered. In Germany **extraction under pressure** is often made in large copper pans and at a raised temperature. After being in contact with the material for the desired length of time the liquor is pumped into the next pan, and in this way it is possible to obtain by only three waters liquors up to 90° Bkr., and a spent tan with only 1 per cent. tannin. The plant is very expensive, however, and only pays for large factories.

Sprinkler leaches, once used to some extent in the United States, are so arranged that the material for extraction is placed in a vat and sprayed on the top at the same rate as the liquor is removed from the vat, but the complete exhaustion of the material in this way is exceedingly difficult, and the loss in tannin due to oxidation is very considerable.

Extract Manufacture.—In this industry the extraction is carried distinctly further than in ordinary leaching, especially when the material being extracted contains only a comparatively small amount of tannin. Hence it is often necessary to decolorise afterwards in order to remove the colouring matters which have been formed and extracted by the higher temperatures and the more thorough infusion employed.

Where wood is the source of the tannin, the larger branches are stripped of bark and stored for a few months until the resinous matters become insoluble, and, after cutting into small logs, are shredded in a mill. The extraction is made in large deep circular vats, which have a copper coil below the false bottom running round three times and passing several inches up the centre of the vat, where it is covered by a copper funnel. The vats have thick oak removable lids, protected against spurting by a copper bell. After two hours' boiling on the first lot of wood, the liquor is pumped on to a fresh lot in another vat, and so on. When the liquor comes out of the last vat it is generally about 3° Bé, and very dark, because of the metallic "tannates" it contains. Sulphuric acid is

sometimes used in the extraction to obviate this, but excess is carefully avoided. Fresh waters come over the partially spent wood, and after one or two changes it is quite spent. After extraction, the liquor is allowed to settle in tanks, and the clear liquor run off from the reds, fibre, resinous matters, etc.,

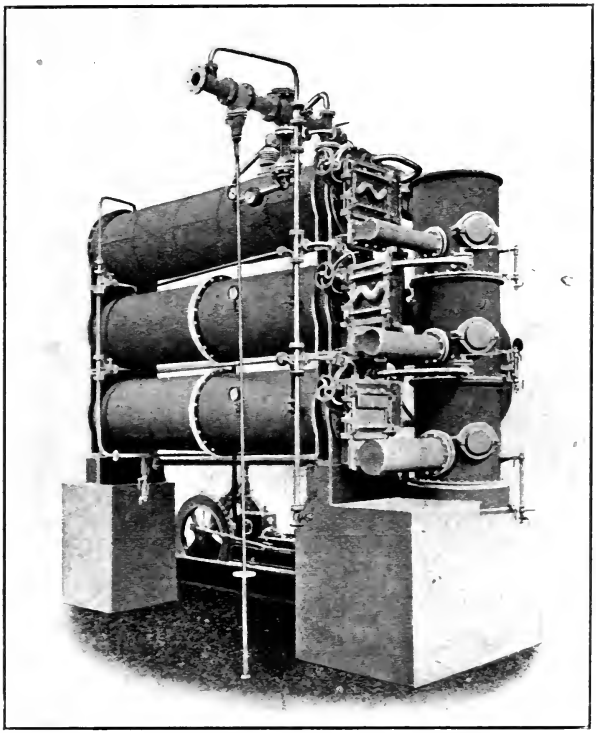


Fig. 55.—Yaryan evaporator.

into a brewer's cooler, which brings the temperature down to about 55° C. The liquor is now run into the decolorising plant, which consists of a deep vat with a false bottom, a coil of pipes beneath this to raise the temperature, and a mechanical stirrer, attached to power. Many substances, such as lead acetate, alum, casein, potassium ferrocyanide, oxalic acid, etc., have been suggested as decolorising agents, but

none are so good as the originally used material—blood albumin. The bullock's blood, or "blood crystals," dissolved in water, is run into the vat and well mixed. The vat is now heated up to 70° C.; the albumin coagulates and carries down with it much of the colouring matter and some little tannin. After standing for an hour or two, the clear liquor is then gently run off by means of taps fixed at different heights in the sides of the vats, and passed into the evaporating plant. The sediment is run off separately and passed through filter presses which yield more liquor for evaporation, and solid cakes of albuminous matter which can be sold for manure. The evaporation is carried out in steam-heated vacuum pans, in order to keep the temperature low and to prevent oxidation. The Yaryan apparatus (Fig. 55) is very suitable for this purpose, the evaporation being quickened by conversion of the liquor into spray by admission into steam-heated copper tubes, these passing into a separating chamber at the other end, kept at a low pressure by an air pump. The steam formed from the evaporation of the first liquor, after straining from any spray, is often used to heat up a second arrangement of pipes maintained at a lower pressure, and so double, triple, and multiple effects may be obtained. It is not possible to concentrate much beyond 25° Bé with this apparatus, so that it is necessary to finish off in ordinary vacuum pans, and where solid extracts are being manufactured these last pans should be broad and shallow and have a wide exit, as the evaporation is continued until the extract will only just run out into the cooling boxes, and may be accidentally taken too far. Sulphited extracts are made, chiefly from quebracho and hemlock (*see* p. 136), by heating with sodium bisulphite in closed vessels. Sulphurous acid is evolved, and the base combines with the reds, which are thereby made soluble and available for tanning.

The use of extracts in the tannery has very largely increased in recent years in spite of much early prejudice. They save much cost and trouble in preparing the liquors, and strong liquors can be made from them without difficulty, and of definite strength. Better colour is also obtained from many extracts than by the ordinary leaching of the material

from which they are made, and many new materials, such as oakwood and chestnut wood extracts, are now on the market which the tanner would never have thought of preparing himself, on account of their poor strength in tannin. Extracts should always be bought on analysis by the standard method, and are best dissolved in warm water (40° to 60° C.) when making up the liquors

CHAPTER XIII

THE PRINCIPLES OF VEGETABLE TANNING

The principles involved in the vegetable tanning processes require very careful consideration, for they largely determine both the nature of the resulting product and the economical manufacture of that product. All vegetable tannages consist in immersing the goods in aqueous infusions of the vegetable tanning materials, and in allowing the penetration of the tannins into the hides, on the corium fibres of which they act so as to give an insoluble and imputrescible product. The penetration involves probably both chemical and physical actions, and has often associated with it also the mere mechanical deposition of other insoluble matters, *e.g.*, bloom, reds, etc., which are in no way chemically fixed in the hide. The completeness of this penetration is a matter in which there is considerable variation; in some cases the hide fibres are merely coated with the tannin, whilst in others the penetration is thorough and even. In all tannages the most important maxim is to start the tanning in weak infusions and afterwards to move the goods through other liquors in which the tannin strength is gradually increased. With hides, the penetration is practically only due to the diffusion of the tanning liquor, and as the exterior is first tanned the interior of the hide is somewhat protected, hence the necessity arises of increasing the concentration of the diffusing liquor so that the penetration may be maintained at an appreciable rate. The rate of this increase in tannin strength is an excessively important factor in determining the nature of the leather which will be obtained. If the strength of the liquors be increased rapidly the penetration through the hide will be considerably quickened, but the penetration of the tannin through the hide fibres is very liable to be incomplete, and the grain tends to be rough and harsh, and in extreme cases

will be "drawn" and wrinkled. When the difference in the strength of the liquors is very great the exterior may be tanned so hard that it is quite impossible, even with longer time, to penetrate into the untanned portion. All these points are well illustrated in many drum tannages. If, on the other hand, the rate of increase in tannin strength is very small, a longer time is needed for the tannin to "strike through" the hide, and indeed for the whole tannage, but the fibres are more completely tanned and a smooth grain can be obtained with very much less difficulty. This is well illustrated in a long oak bark tannage in weak liquors. If goods are placed in liquors of less strength than those from which they have just been taken, the gradually decreasing concentration of the liquor in the hide is considerably disturbed and with difficulty re-established. The nature of the tannins being used has also a great influence. The astringent tannins (*e.g.*, quebracho) are very liable to draw the grain in the early stages if used in too great a concentration, but if used in weak solution will strike quickly through the hide, but not so thoroughly through the fibre. The less astringent tannins (*e.g.*, myrobalans) can be used in stronger solutions and the rate of increase may be greater; their penetration through the hide is much more even, but usually slower.

From these considerations it will be clear that to obtain a thorough and quick tannage the best way is to use the less astringent materials in the earlier stages and to assist their penetration by a certain amount of motion, and afterwards, when the grain is fixed, to use stronger liquors containing the more astringent tannins. This is usually accomplished in practice by working the liquors gradually down the yard. As the goods pass through the liquors their astringency as well as their strength decreases, because the more astringent tannins are in preference absorbed by the hides, and hence, by employing such used liquors for the next earlier stage in the tanning, a series of liquors are obtained where tannin is gradually being absorbed and whose action is becoming increasingly "mellow." The increasing quantities of calcium and other salts in these liquors and their greater proportion to the weak acids present has also been demonstrated to be

an important factor in producing mellowness. The usual procedure, therefore, is to place the hides at first in old and nearly exhausted liquors and gradually to move the goods through newer and stronger liquors. It is obvious that this method of manipulation is economical as well as scientific. Another point for an economical tannage is the desirability of keeping the volume of the tanning liquor in as small a ratio to the quantity of hides as is consistent with easy manipulation and good results.

The quantity of free acid in the tanning liquors is a matter of the first importance, for practically all tanning liquors contain these acids in some degree. They are weak organic acids (lactic, acetic, etc.), derived from the sugars associated naturally with the vegetable tanning materials and play an exceedingly important part in the tannage. They tend to swell the hide fibres and thus act in the opposite direction to the tannins, so that the important matter is to have a correct ratio of acid to tan throughout the whole yard, but especially in the earlier stages. This ratio differs widely for different classes of goods, and is largely influenced by the condition of the hides when entering the tan liquors, which is determined by the nature and extent of the deliming process. Hides in a plumped state tan more slowly than in a fallen condition, but absorb a greater amount of tanning matter and yield a firmer and more inflexible leather. Hence butts for sole leather practically always enter the tanning liquors with a certain amount of caustic lime in them, this being later neutralised by the acids in the liquors which are kept in excess, not only to prevent the formation and oxidation of lime tannates (cp. p. 46), but also to maintain the goods in a plump condition. If the butts are delimed merely by washing in water for a short time, the acidity of the first suspender liquor (which in a regularly worked tannery indicates generally the degree of sourness of the whole yard) should correspond to nearly 10 cc. of lime water when determined by Procter's method (p. 154); but if a bath of boric acid is used to remove all the surface lime and half the total the acidity may safely go down to that corresponding to 4—5 cc. of lime water, though this matter is somewhat influenced by

the nature and strength of the liquor. With dressing leather goods and skins, which are delimed uniformly and completely, the acidity is, generally speaking, less than in the sole leather tannages, because more flexible leathers are required, and the more unswelled and fallen the goods are in the early stages of tanning, the softer the product obtained. Where extracts are much used and the liquors worked quickly down the yard, the natural acidity or "sourness" of the first liquors may not be so great as is desirable. These "sweet" liquors must then be artificially acidified by the addition of lactic and acetic acids, or by an increased use of myrobalans or other acid-forming materials.

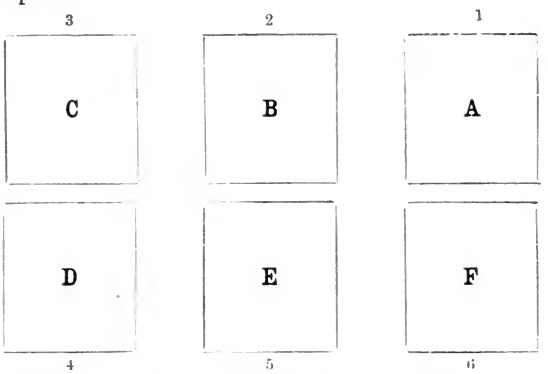
The amount of motion given to the goods in tanning influences not only the rate of penetration, but the nature of the resulting grain, and the tan-yard liquors are usually divided up into distinct sections in which the mechanical operations are different and distinct. The first pits entered by the goods containing the old mellow liquors are called the "**suspenders.**" The goods are hung vertically in these liquors by means of hooks or strings, or by placing over poles. In these pits the acid penetrates into the hide, neutralising any remaining lime and plumping the pelts, thus preparing the way for the more slowly penetrating tannins. In these pits evenness of action of both acid and tannin and a good light colour are some of the chief points to be aimed at, and these are best obtained by a frequent shifting of the goods. Hence each pack is usually shifted once each day, and in the first suspender liquors the goods are often kept in constant motion by suspending in wooden frames, which are rocked gently either by a horizontal to and fro motion or by a rotatory up and down motion, in which latter case each half of the pack is alternately partly removed from the liquor. The frames are worked with overhead shafting attached to power. A series of such pits are often termed "**rockers.**" When a quick and even colouring is desired, as in the case of some dressing leathers and many skins, the goods may be **paddled** in the first liquors; but this should not be done when firmness is important, as in sole leather, or where a smooth grain finish is desired, as the constant bending of the goods works up the

grain pattern in a manner somewhat similar to some of the finishing processes. Where a "grain" is afterwards to be worked up, however, it is sometimes desirable to start the tannage in a rather strong liquor to draw the grain slightly. This may be done in paddle or in pit, the goods afterwards entering ordinary weak suspenders. A method of working these liquors which is sometimes convenient is to arrange them like a press leach, except that the liquors should press upwards. The weakest liquor is each day run down the drain, and liquor from the later stages is pumped into the top pit of the battery which presses on and refills the tail pit. Usually, however, the suspenders are worked in "rounds" in which the goods receive a definite number of liquors of definite barkometer strength. The fresh liquor is made up each day from the weakest liquors from the handlers, and is gradually worked through the round until it becomes the tail liquor and is run away.

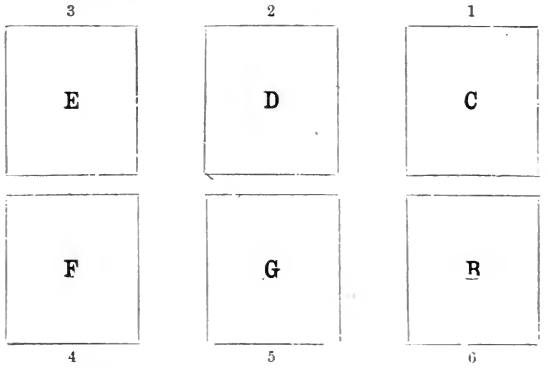
The **handlers** are the next liquors, and are also worked in rounds. In these pits the goods are laid horizontally one above the other, grain side uppermost, and allowed to lie perhaps two or three days without being shifted. The strong liquor is made up from the old layer liquors or leaches, and after working through the round till it forms the weakest liquor, is then used as the source of the head suspender liquors. In the forward handlers ground bark, myrobalans, algarobilla, etc., are often "dusted down" with the goods as they are placed in the liquors, a little being put in between each hide or butt, or sometimes a separate round of pits is used in which this treatment is given. Such pits are termed **dusters**, while the term **floaters** is applied to those pits in which clear liquor only is used.

It is obvious that the arrangement of all these pits and rounds is a matter in which there is considerable scope for variation, and for adjustment to the local convenience and the character of the tannage, but it might be instructive to show the working of a round of handlers in order to illustrate generally the nature of the mechanical operations in the tan yard. If a round of six pits are in use, let A be the pack in the strongest liquor in pit 1, and F the "green" pack which

has last come from the suspenders and lies in the weakest liquor in pit 6.

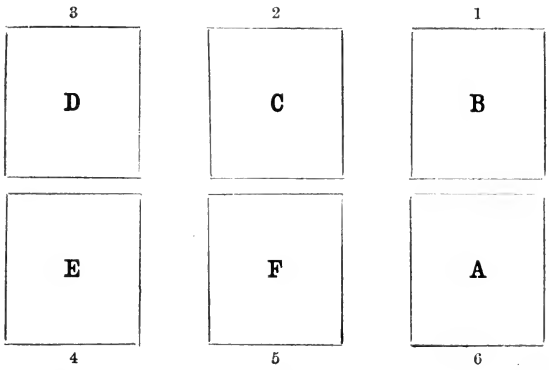


The procedure is then as follows: Pack A is hauled and taken to the dusters or layers, pack F is next hauled and the liquor pumped away to form the head suspender. In pit 6 is now made up the new head handler liquor, and pack B is hauled from pit 2 and put into it; pack C is put into pit 1, which is now the second best liquor; pack D is shifted into pit 2, pack E into pit 3, pack F into pit 4, and the new green pack G, from the suspenders, is placed in the weakest liquor in pit 5. The arrangement is now thus:—



If on the other hand no green pack enters and no tan pack leaves the round, and the goods are to be shifted and a new liquor made, the pack F in the weakest liquor in pit 6 is hauled, the new liquor made in that pit, and the goods moved

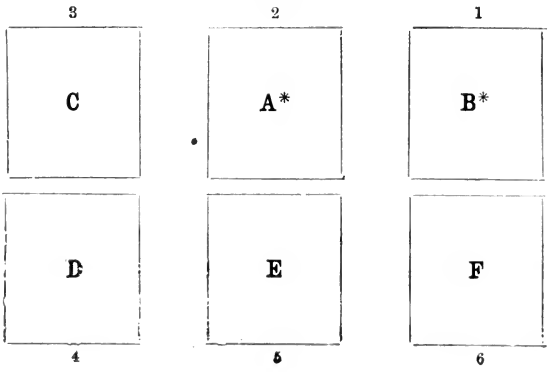
forward merely into the next pit, the tan pack A into the new liquor in pit 6, pack B from pit 2 into pit 1, and so on, the green pack first hauled going into pit 5. The position is then thus :—



It is evident that either of these changes may be worked once a day or once every two days, and that they may be worked on alternate days.

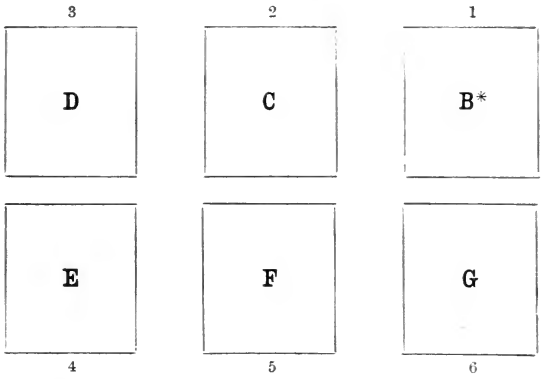
In cases where a round of handlers contains both floaters and dusters, it is desirable that the goods in the latter should lie undisturbed for a longer period than those in the former. If, for example, in a round of six handlers, the goods are dusted down in the head liquor, and if a green pack enters and a tan pack leaves the round every two days, one liquor being given also every two days on the day on which no pack is received, let the position be the following :—

Position I.



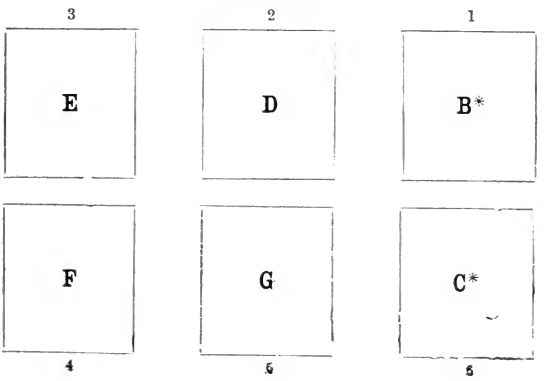
The mode of procedure is then as follows: the "tan" pack A comes out of its duster and is taken to its layers, the next pack B (which is in its duster) is not disturbed, but the remaining packs C, D, E and F are given a single shift forward, and the new green pack G from the suspenders is placed in the weakest liquor in pit 6. The arrangement is now as follows: —

Position II.



On the next day the green pack G is hauled, the liquor in pit 6 run to the suspenders, and a new liquor made in that pit. Pack C is now hauled and dusted down in pit 6. The rest are given a single shift forward, thus :—

Position III.



If it be desired to save handling and tan-yard labour, both these changes may be carried out on the same day, and the goods left undisturbed on alternate days. The new liquor is given and the duster made on the same day as the tan pack leaves and the new green pack enters the round. Pack C is then given a treble shift and enters its duster immediately in pit 6, the rest receive a double shift, and the green pack G enters pit 5, which now contains the weakest liquor. The goods, therefore, change from Position I. directly to Position III. In this case the round always contains two dusters, but each pack only receives half the number of liquors.

If one pack is received and lost each day, and a new liquor given each day, the change is also direct from Position I. to Position III., but takes place each day, and in this case the goods pass through the round in half the time taken by the preceding cases.

In the case where one pack is received and lost every two days, and a new liquor given each day, there are two liquors for every pack. The method of working is then to give the change from Position I. to Position II. on one day, and the double change every second day, similar to the change from Position I. to Position III.

Similar methods of working can be of course used for rounds of eight, ten, twelve or more pits, with three or more dusters in the round, the general principle being that the tan pack is always in the pit next to the strongest floater. These methods of working a round of handlers are often common in dressing leather yards, but no dust is given, and the "dusters" are therefore termed "**liquor packs.**"

The handling forward of goods is best done by hand labour; but "reels" have been employed, in which case the goods are strung together and wound over into the next pit. This is rather quick, but is really only suitable treatment for offal. An overhead crane has also been used to some extent.

Goods are worked through handlers to flatten and straighten them by virtue of their own weight. It is a less convenient method for handling the goods than suspension, and the goods also do not "feed" so well. In many modern yards therefore it is found more convenient to put the goods in handlers for a

sufficient time to set the fibres flat and to ensure the absence of creasing and buckling, and then to put the goods again in suspension. Rounds of such pits may be worked like a handler round, and are often termed "suspender-handlers."

The "**layers**" or "layways" are pits used for the heavier leathers in which much stronger liquors are used, a greater amount of dusting material employed, and in which the goods are allowed to lie undisturbed for a decidedly longer time. They are made up from the leaches, strengthened where desired with extract and solid material, and are afterwards used as the source of the head handler liquors. The principal function of these pits is to give time for a complete tannage of the hide fibres, a thorough penetration of the liquor, and to give weight and firmness to the leather by the deposition of bloom, reds, etc., in the interior of the hides. In this stage only one or two pits are necessary, the goods being hauled at certain intervals and dusted down again in the same or a new liquor with further quantities of fresh material.

Generally speaking, the shoulders and bellies of rounded hides have their own suspenders, handlers and layers, but are sometimes taken with the butts through the whole or part of the suspender stages, and occasionally through the handlers.

In the tannage of skins for lighter leathers the general principles as explained above still apply. The suspenders are largely replaced by paddles, which ensure even penetration and colour. The handler liquors need not be of such great strength as in tanning hides, because the goods are thinner and the complete penetration therefore quicker, whilst at the same time the *weight* of the resulting product is usually of no consequence. For the same reasons the long layers are not needed, the skins being often finished in paddle in order to obtain softness and good colour. Where a quick tannage is desired the bottle or bag tannages are sometimes employed, in which the skins are sewn up to form a closed vessel in which tanning liquor is placed and is forced through either by mechanical pressure or by the pressure of its own weight.

In drum tannages also the general principles of tanning are the same, the particular object in drumming being to bring

about a quick penetration of the liquor and a rapid tannage. The tanning strength of the liquors is increased at a much more rapid rate than in the pit tannages, the final liquors being often neat extract. It is usual to pass the goods through suspenders for a few days before entering the drum liquors in order to fix the grain, but some processes claim to avoid this by short suspensions in solutions of formaldehyde, boric acid and other materials. In all cases, even for sole leather, the goods should be completely delimed and thoroughly scudded, the former because the acidity of extract liquors is so small, and the latter to assist in quick penetration. The tannage is essentially with extracts, but that from chestnut wood is about the only suitable one, being a mellow, quickly penetrating and fair weight-giving tannin. Treated quebracho extracts, hemlock extracts, and oakwood extracts, have, however, been employed in conjunction with chestnut extract in the stronger drum liquors.

Both hides and skins are often "split" (see p. 277) when half tanned or "struck through"; the "grains" then go forward with the ordinary tannage, whilst the "splits" receive a much cheaper and inferior tannage, often in drums. "Degreasing" may also be done before the tannage is complete.

CHAPTER XIV

THE TANNAGE OF SOLE LEATHER

In the tannage of any clsss of leather it is impossible to specify a method which is in quite general use, for the methods employed differ in almost every tan yard. Hence the practical methods which are given in this and the following chapters must be taken merely as typical processes, which have been found to yield good results, but which may be varied in many directions according to local circumstances. Broadly speaking, there are in this country three classes of methods which are in common use for the tannage of sole leather—the oak-bark tannage, which is the oldest process, the West of England tannage, of which valonia is the chief material, and the modern mixed tannage in which many tanning materials are blended together. In the United States also there are three chief varieties of sole leather tannage—the oak tannage, the hemlock tannage (acid and non-acid), and the union tannage, in which a combination of oak and hemlock is used. Another different class of tannage employed in both Europe and America is the quick drum tannage in extracts. These will now be dealt with in more detail.

The oak-bark tannage, in which the best Continental and Scotch hides are mostly employed, lasts about twelve months and is brought about in comparatively weak liquors. The barkometer strength of these is very variable, according to whether the used liquors are re-strengthened by pumping again through the leaches or worked down the yard. In the former case there is a gradual accumulation of non-tannins in the liquors, so that although the tanning strength may not be widely different from the other method, the barkometer strength appears greater. In a pure oak-bark tannage, where the liquors are worked down the yard, about the strongest liquors obtainable are of 20° Bkr. strength, but where the liquors are constantly strengthened up in the leaches the strongest liquors may go up to about 35° Bkr. In most

modern oak-bark tannages a certain proportion of valonia, gambier and sometimes other materials are used and stronger liquors obtained. This is illustrated in the following typical tannage.

The goods (*e.g.* 100 butts) after deliming and scudding go into the **suspenders**, in which they are hung by strings over poles in liquors, which run usually from 10—18° Bkr., though the weakest may be taken as low as 6° Bkr. Here they remain 16 to 18 days, being handled forward each day to the next pit, and hauled frequently or rocked in the first two days. They then go into the **handlers** (floaters) for a month, being moved every day in the first fortnight and every second day in the second fortnight. A series of 12 pits are used, ranging from 18—24° Bkr. The head handler is a 20° Bkr. liquor from the dusters or leaches made up to 24° Bkr. with gambier. The butts now go into the **dusters**, a series of seven pits, in each of which the goods lie for one week. The first four dusters are about 24° Bkr., and the goods receive 3½ cwt. of bark dust; the next three pits are about 26° Bkr., and each pack is dusted down with 3 cwt. bark and 1 cwt. myrobalans. The goods now go to the **layers**, which are shown as follows:—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	30°	3	4 cwt. bark.
2nd	33°	4	4 cwt. bark (light butts now go to sheds).
3rd	38°	4	4 cwt. bark.
4th (for mediums)	40°	4	4 cwt. bark and ¼ cwt. valonia (medium butts now go to sheds).
4th (for heavies)	40°	4	4 cwt. bark and ½ cwt. valonia.
5th (for heavies)	45°	6	4 cwt. bark and 1 cwt. valonia (heavies now go to sheds).
6th (for extra heavies)	50°	6	4 cwt. bark and 1 cwt. valonia (extra heavies now go to sheds).

Mimosa bark may be added to the leaches, and a small amount of extract employed where it is necessary to bring up the strength of the new liquors. The shoulders go through

the suspenders and handlers with the butts, but have their own layers as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	26°	1	3 cwt. bark.
2nd	27°	1	3 ,, ,,
3rd	30°	2	4 ,, ,,
4th	34°	4	4 ,, ,,

The **bellies** have a set of liquors of their own, made by leaching the fishings from the dusters and layers. They are 14 days in **suspenders**, ranging from 10—20° Bkr., 14 days in **handlers**, ranging from 20—25° Bkr., and then go (250 pairs being taken) to the **layers**, which are as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	25°	1	4 cwt. bark.
2nd	26°	2	4 ,, ,,
3rd	28°	3	4 ,, ,,
4th	32°	4	An old butt layer liquor and 4 cwt. bark.

A little gambier is used in making up the first three belly layers.

The rate of tannage by this oak-bark process has been investigated,[1] and the results obtained by the analysis of the butts at various stages in tanning are shown in the Table on p. 182.

The West of England tannage of heavy South American salted hides lasts about 9 months and is carried out as follows :—

The butts (100) are in **suspenders** for three weeks ; the liquors range from 20—40° Bkr., but consist largely of non-tannins. They then go to the **handlers** for four weeks, the best liquor of which is obtained from the old dusters, and is made up to strength with ½ ton of gambier. The pits run from 40—55° Bkr. Four **dusters** at 60° Bkr. are now given, and the packs allowed to lie a week in each, handling twice. These liquors are made up either from the old hemlock liquors or

[1] J.S.C.I., 1902, 839.

OAK BARK TANNAGE: 10 MONTHS.

—	Hide Substance.	Tanning.	Mineral Ash.	Moisture.	Tannin absorbed per 100 parts of Hide Substance.	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.		
End of 24 hours	80·9	2·8	2·3	14·0	3·4	
,, 2nd day	79·0	5·1	1·9	14·0	6·4	
,, 4th ,,	76·6	7·8	1·6	14·0	10·1	Suspenders.
,, 8th ,,	71·6	13·5	0·9	14·0	18·8	
,, 18th ,,	60·0	25·4	0·6	14·0	42·3	
,, 25th ,,	56·3	29·1	0·6	14·0	51·6	
,, 32nd ,,	55·1	31·3	0·6	14·0	56·8	Handlers.
,, 46th ,,	53·4	32·0	0·6	14·0	59·9	
,, 88th ,,	49·0	36·3	0·7	14·0	74·6	End of 6 weeks in dusters.
,, 102nd ,,	47·3	38·0	0·7	14·0	80·3	1st layer.
,, 132nd ,,	46·5	39·9	0·6	14·0	87·6	2nd layer.
,, 162nd ,,	44·1	41·2	0·7	14·0	93·4	3rd layer.
,, 192nd ,,	43·4	42·0	0·6	14·0	96·7	4th layer.
,, 234th ,,	42·6	42·8	0·6	14·0	100·4	5th layer.
,, 278th ,,	41·6	43·8	0·6	14·0	105·2	6th layer.
,, 290th ,,	45·3	40·1	0·6	14·0	88·5	Washed up in weak liquor.
	46·5	38·9	0·6	14·0	83·6	Scoured by machine.
	47·2	39·2	0·6	14·0	83·0	Brushed and pinned by hand.
,, 310th ,,	47·0	39·4	0·6	14·0	83·8	Finished leather.

from a 40° Bkr. fresh myrobalans leach liquor and several casks of hemlock extract. The latter course gives the better colour. The goods are dusted down with $1\frac{1}{4}$ cwt. bark and $1\frac{1}{4}$ cwt. myrobalans. The packs now receive a **hemlock round** of four liquors at 60° Bkr., made up entirely from hemlock extract. They lie a week in each liquor and then enter the **layers**, which are as follows:—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	60°	2	2 cwt. oak bark and 2 cwt. valonia.
2nd	65°	2	4 cwt. valonia.
3rd	70°	3	4 ,, ,,
4th	75°	4	5 ,, ,,
5th	80°	4	6 ,, ,,
6th	90°	6	6 ,, ,,

Sometimes an extra layer is given and the valonia partially substituted by myrobalans in the early layers. It is usual also to employ a certain amount of oakwood extract in making up the strong layers.

The rate at which the butts are tanned by this process has also been investigated[1] analytically, and the following results obtained :—

WEST OF ENGLAND TANNAGE; SOUTH AMERICAN SALTED HIDES; 10 MONTHS.

—	Hide Substance.	Tanning.	Mineral Ash.	Moisture.	Tannin absorbed per 100 parts of Hide Substance.	—
	Per Cent.	Per Cent.	Per Cent.	Per Cent.		
End of 1st day	78·4	4·2	3·4	14·0	5·3	Suspenders.
„ 2nd „	75·8	8·2	2·0	14·0	10·8	
„ 4th „	74·0	10·4	1·6	14·0	14·0	
„ 8th „	65·9	19·1	1·0	14·0	28·9	
„ 21st „	58·3	26·8	0·9	14·0	45·9	
„ 28th „	53·8	31·3	0·9	14·0	58·1	Handlers.
„ 35th „	51·8	33·4	0·8	14·0	64·4	
„ 56th „	49·2	36·0	0·8	14·0	73·1	
„ 88th „	44·2	41·0	0·8	14·0	92·7	Dusters.
„ 112th „	41·0	44·2	0·8	14·0	107·8	Hemlock round.
„ 126th „	40·8	44·4	0·8	14·0	108·8	1st layer.
„ 147th „	39·6	45·6	0·8	14·0	115·1	2nd layer.
„ 177th „	38·0	47·1	0·9	14·0	123·9	3rd layer.
„ 208th „	37·2	47·9	0·9	14·0	129·0	4th layer.
„ 238th „	36·5	48·7	0·8	14·0	133·4	5th layer.
„ 270th „	35·9	49·2	0·9	14·0	137·0	6th layer.
„ 300th „	34·7	50·4	0·9	14·0	144·9	7th layer.
„ 302nd „	38·9	46·2	0·9	14·0	118·4	Washed in weak liquor to cleanse.
	39·7	45·5	0·8	14·0	114·5	Scoured under machine.
	39·6	45·5	1·1	14·0	114·6	Finished. Product after oiling, colouring, rolling and drying.

The modern mixed tannage of salted Continental, Scotch and English marked hides last only about 4—5 months, and may be carried out in the following ways :—

[1] J.S.C.I., 1902, 839.

Process (*I.*).—The butts (100) go into **suspenders** (20—40° Bkr.) for about a week, rocking in the first liquors. The goods are handled forward to a new liquor each day. The **handlers** (40—55° Bkr.) are now entered, rounds of eight pits being employed, the two most forward of which are **dusters**. The

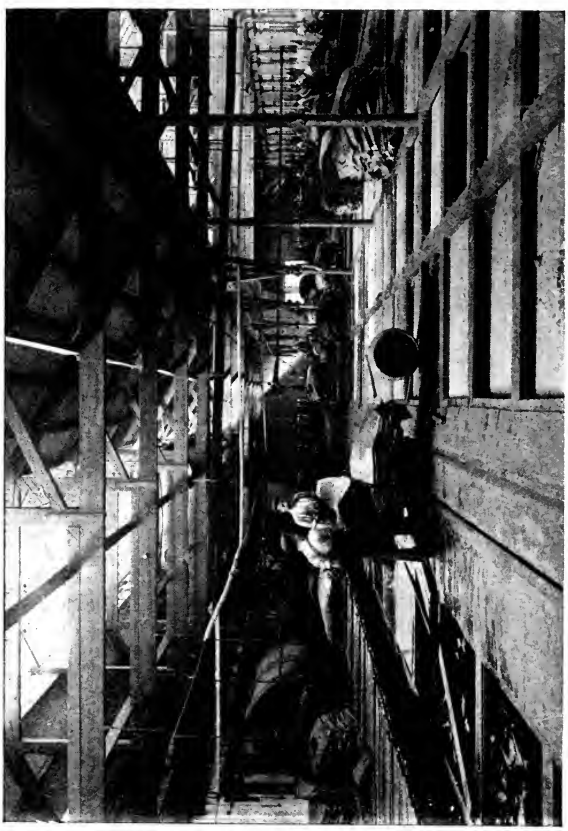


Fig. 56.—Tan Yard (Messrs. Walker, Ltd., Litherland).

best liquor is obtained from the layers, and the goods are dusted down with $1\frac{1}{2}$ cwt. of myrobalans (or a mixture of myrobalans and algarobilla). The goods remain a fortnight in these liquors and should then be struck through. They now proceed to the **suspender handlers** (55—65° Bkr.) in which they remain 2 or 3 weeks, handling forward on alternate days.

The head liquor is made up from fresh leach liquors and chestnut extract. Four layers are given as follows :

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	70°	1	4 cwt. myrobalans.
2nd	75°	2	4 cwt. valonia.
3rd	80°	3	4 cwt. of valonia and 3 casks chestnut extract.
4th	90°	4	4 cwt. valonia and 4 casks oakwood extract.

The third and fourth layers are made up of fresh leach liquors (65° Bkr.) made from the fishings ; the second layer is an old fourth layer liquor and the first layer an old third liquor. The fishings go to the leaches, and the clear liquors from the old first and second layers are pumped chiefly to the handlers but partly to the offal pits. As chestnut extract and myrobalans are used in one pit, and oakwood extract and valonia in the other, it is desirable to mix these in a large pit before pumping to the handlers, and if the liquor is too strong it should be weakened with a 40° Bkr. liquor from the leaches, and any other materials (*e.g.*, quebracho extract) may also be added at this stage. A little mimosa dust may be added to the first layer, the valonia partially replaced by myrobalans in the second, and a blend of oakwood and chestnut extracts (2 : 1) may be used in the third and fourth layers.

Another method for working the layers is as follows:—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	80°	2	4 cwt. myrobalans.
2nd	85°	2	4 cwt. myrobalans and chestnut extract.
3rd	90°	3	4 cwt. valonia and 4 casks oakwood extract.
4th	100°	4	4 cwt. valonia and 4 casks oakwood extract.

The first layer liquor is an old fourth layer liquor in which the goods are handled three times in the first 10 days and

dusted down with the myrobalans for the rest of the time. The second liquor is an old first liquor strengthened with extract, the goods being dusted down at once for the whole time. The third liquor is made up from the leaches with the help of extract, and the fourth liquor is an old third liquor re-strengthened with extract. In this case therefore only one pit is used, and the old second liquor used entirely for the butt handlers, and the fishings are leached for the offal.

Yet another method is as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	70°	1	Old fourth liquor, no dust, liquor goes to handlers.
2nd	75°	2	New liquor from leaches, and extract.
3rd	85°	3	Old second strengthened with extract.
4th	95°	4	Old third strengthened with extract.

The offal is usually taken through separate liquors, though the shoulders sometimes go through the suspenders with the butts. A common method is to **colour** the shoulders and bellies in latticed drums, using old butt suspender liquors. They then go into **suspenders** (18—40° Bkr.) for 4 to 5 days, and the shoulders are now put into the **shoulder-handlers** (40—55° Bkr.) The packs (200 in each) are handled forward each day for three weeks, and in the head liquor, which is made up each day, 2 cwt. of myrobalans are used as dusting material. The **shoulder layers** are as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	60°	2	3 cwt. myrobalans.
2nd	65°	3	3 cwt. myrobalans and chestnut extract.
3rd	80°	4	2 cwt. myrobalans, 1 cwt. valonia and chestnut extract.

The first liquor is an old third liquor, the second a new leach liquor strengthened with extract, and the third liquor is an old second liquor, fished and raised to 80° with chestnut extract.

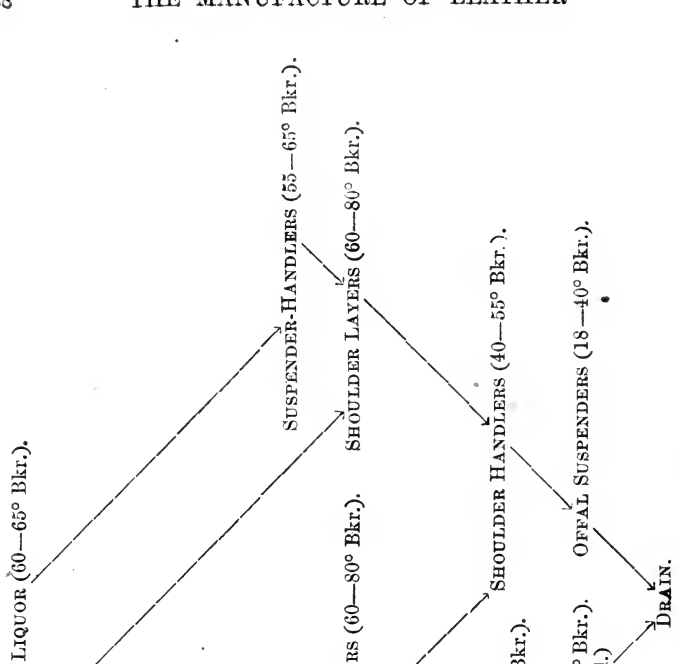
The bellies (250 pairs) go through the shoulder handlers for a fortnight and then go to three layers of one week each, being 60°, 70° and 80° Bkr. strength, and having myrobalans as dusting material. In another method they receive 4 days in **suspenders**, 4 days in 4 **handler** pits (40—60° Bkr.), and then go to the **first layer** (70° Bkr.), for one week, using 4 cwt. myrobalans. They are then drummed in the first layer liquor made up to 80° Bkr. with chestnut extract. A little mimosa dust is added and the drumming continued for four hours in different parts of the day. The goods are then firmed up by a **second layer** (100° Bkr.) for 3 or 4 days.

In leaching for a mixed tannage such as the one just described, *only* the fishings from the layers should be used. These will seldom yield a liquor of more than 65° Bkr. strength, and it is usual to employ the head leach as the source for making the yard liquors (ctr. dressing leather, p. 198). The liquors are worked down the yard as shown in the diagram on p. 188.

Process (*II.*).—In this tannage the butts were delimed with 20 lbs. boric acid per 100 butts. The tannage consists of one-third extract, one-third valonia, the remaining third being chiefly myrobalans, but with smaller quantities of mimosa bark, quebracho, algarobilla, etc. The butts (100) are in *rockers* (20°—45° Bkr.) for 4 to 6 days, being of course in suspension. The *handlers* (45°—60° Bkr.) are large rounds including several dusters, and the goods remain in these liquors 4 to 5 weeks. In the *dusters* the butts receive 2—3 cwt. myrobalans. The *layers* are as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	65°	1	4 cwt. myrobalans and chestnut extract.
2nd	70°	2	2 cwt. myrobalans, 2 cwt. mimosa bark and chestnut extract.
3rd	80°	3	4 cwt. valonia } and oakwood extract.
4th	90°	4	4 „ „ }
5th ("heavies" only)	100°	6—7	5 „ „ }

Mix the quebracho and gambier in the handlers.


Best Leach Liquor (65° Bkr.).
4th Butt Layer (90° Bkr.).
2nd Butt Layer (75° Bkr.).
2nd or 3rd Leach Liquor (60—65° Bkr.).
3rd Butt Layer (80° Bkr.).
1st Butt Layer (70° Bkr.).
Mixing Pit
(+ 40° Bkr. Leach Liquor).
Suspender-Handlers (55—65° Bkr.).
Shoulder Layers (60—80° Bkr.).
Belly Layers (60—80° Bkr.).
Handlers (40—55° Bkr.).
Shoulder Handlers (40—55° Bkr.).
Suspenders (20—40° Bkr.).
Latticed Drums (18° Bkr.).
(For colouring offal.)
Offal Suspenders (18—40° Bkr.).
Drain.

Process (*III.*).—Another mixed tannage may now also be outlined in order to illustrate further the possible variety in methods of procedure. In this case the tannage only lasts about four months. The butts are given 8 days in **suspenders** (10—25° Bkr.) handling twice a day and handling forward each day, and then pass into a round of **handlers** (30—45° Bkr.) for four weeks. The two head liquors of this round act as dusters, 1 cwt. of myrobalans dust being used. If necessary the head liquor may be strengthened with quebracho. The **layers** are as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	60°	1	Mimosa bark and myrobalans.
2nd	70°	2	Myrobalans and valonia.
3rd	75°	3	Valonia.
4th	90°	4	Valonia.

In "vatting" (see p. 261), these goods receive a full week in a liquor (100° Bkr.) made from bright chestnut extract, and are afterwards washed through sumach.

The analysis of the butts at different stages in tanning[1] by this process is given on p. 190.

American sole leather is not rounded but tanned in "sides," or the hides are cut into sides after tannage. **The oak tannage**, lasting about six months, most resembles the British tannages and is chiefly used with native hides. The hides after a short liming (Buffalo method) are delimed and plumped in rockers, and then receive 8 to 14 days in handler liquors. Five layers are given on an average ranging from 30—45° Bkr., and lasting five and a half months altogether. Oak bark (*Q. prinus*) is used as dusting material, and this is also leached to form the liquors. Oak-bark extract is used to make up the strength of the stronger liquors.

The non-acid hemlock tannage is when the only acids used are those formed by natural fermentation. South American dried hides are chiefly used, and after sweating and unhairing are placed in water overnight, and then swollen with acid. They

[1] J.S.C.I., 1902, 840.

MODERN MIXED TANNAGE FOR SCOURED BENDS; 4 MONTHS.

—	Hide Substance.	Tanning.	Mineral Ash.	Moisture.	Tannin absorbed per 100 parts of Hide Substance.	—
	Per Cent.	Per Cent.	Per Cent.	Per Cent.		
End of 1st day	77·5	5·5	3·0	14·0	7·0	
„ 2nd „	74·5	10·0	1·5	14·0	13·4	Suspenders.
„ 4th „	73·2	11·6	1·2	14·0	15·8	
„ 8th „	61·1	24·0	0·9	14·0	39·2	
„ 16th „	53·2	32·1	0·7	14·0	60·3	
„ 23rd „	50·7	34·7	0·6	14·0	68·4	Handler round.
„ 37th „	45·6	39·8	0·6	14·0	87·2	
„ 45th „	41·6	43·6	0·8	14·0	104·8	1st layer.
„ 60th „	39·3	46·1	0·6	14·0	117·3	2nd layer.
„ 81st „	37·8	47·5	0·7	14·0	126·8	3rd layer.
„ 111th „	37·5	47·8	0·7	14·0	127·4	4th layer.
	38·1	47·3	0·6	14·0	124·1	Scoured in machine.
„ 119th „	35·4	49·9	0·6	14·0	140 0	After 1 week in liquor with chestnut extract at strength 100° Bkr.
„ 120th „	38·5	46·7	0·8	14·0	121·2	After washing through sumach bath to brighten colour.
„ 136th „	40·8	44·7	0·5	14·0	109·5	Finished in warehouse.

then go through the handlers (10—16° Bkr.) and then to the layers, which run from 28—36° Bkr. and last about five and a half months altogether. The latter liquors are obtained from the leaches in which hemlock bark is used, and the stronger liquors are made up with hemlock extract.

The acid hemlock tannage is also made chiefly with dried hides—buffalo hides from China being a common material. After sweating and unhairing they are soaked and put into a "colouring vat" containing a weak tanning liquor for ½ hour to 1 hour. They are afterwards placed in a 0·1 to 0·3 per cent. solution of sulphuric acid until plumped to the required extent, and then may be put safely into the first layer liquors, the strength of which differs widely in different yards, but may be even 38° Bkr. The goods are about six

months in the five or six layers, hemlock bark dust and a little hemlock extract being used, and the strongest liquors being nearly 50° Bkr.

A few native hides are limed (and occasionally bated), and afterwards given the acid hemlock treatment. This is called the "slaughter-hemlock" tannage.

The union tannage is by means of both oak and hemlock barks, and yields leather of better texture, colour, and firmness than the hemlock tannages. Salted hides are largely used, and after liming, unhairing, fleshing, and soaking overnight, are put through the handlers. The layers usually receive oak bark only as dusting material and the fishings are leached with fresh hemlock bark to make the liquors.

Much "Union" leather is sold as oak, though tanned with 75 per cent. hemlock. As, moreover, the supply of hemlock bark is now less plentiful, the American methods of tanning are in a transition stage. Quebracho is now very largely employed (sometimes even alone) for making "hemlock" leather. Some tanners employ a mixture of quebracho and mangrove, sometimes along with chestnut extract. Union leather is also tanned with quebracho extract entirely, then bleached and drummed with hemlock extract and glucose. The imports of myrobalans, valonia and mimosa bark into the United States are also rapidly increasing.

The barkometer strengths of all liquors in which hemlock bark is used are very varied in different yards, according to the thoroughness of the leaching. If the leaching is less "close" the liquors have a less barkometer strength; some loss in tannin is incurred, but the colour of the resulting leather is thereby appreciably improved. In the use of both oak and hemlock barks, the used liquors are very often passed again through the leaches to be strengthened, and this also produces considerable differences in the barkometer strengths of the liquors.

In all these tannages also the liquors contain a greater proportion of tannin to non-tannins than in the British methods, and hence the differences in the strength of the layer liquors when the packs are put in and taken out are much greater than in British tannages. The difference in barkometer strength, which is called "sappage," is used as a rough

means of indicating the degree to which tannins have been absorbed, and runs from 20—40° Bkr., according to the strength and purity of the liquors.

Drum tannages, differ considerably in the first stages of the tanning, according to the deliming and preparatory processes that are used, the great aim being to make these processes as short and inexpensive as is consistent with good results. Many patents have been taken for these processes, notably by Messrs. Fratelli Durio, but practically all have

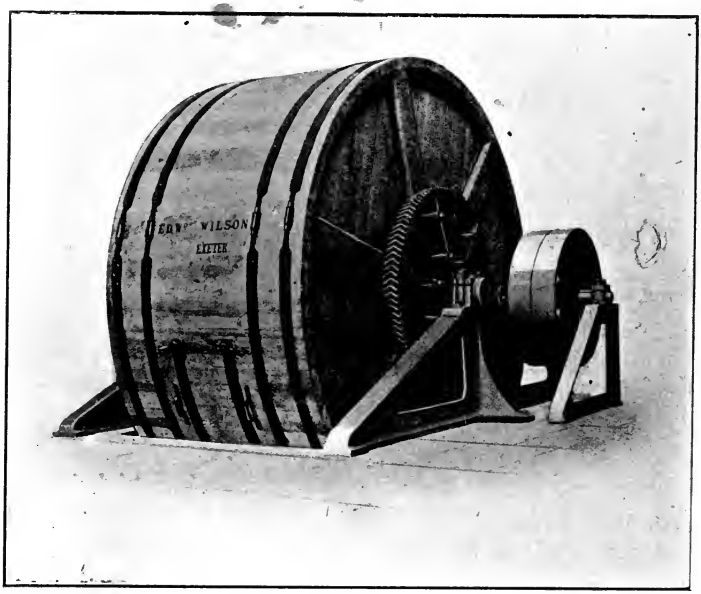


FIG. 57.—Tanning drum.

proved unsatisfactory in the hands of some experimenter, probably owing to insufficient knowledge or attention to the details of the processes in the critical stages, hence many modifications of these patent processes have been made in which the difficulties experienced have been wholly or partially overcome.

The following process has been found to give satisfactory results in some hands. The goods after deliming are suspended for about a week in a round of pits, the liquors of

which have come from the drums. The head suspender is a 30° Bkr. liquor, and is the used liquor from the weakest drums. The goods are struck through in these liquors and then enter the drums in a 7—8° Bé liquor (50° Bkr.). The drums should be quite half full of liquor, and should revolve four to five times per minute, the temperature (which rises because of the friction) being about 30—33° C. The pack should remain in this liquor for twelve hours, and be similarly treated with a stronger liquor, and afterwards with a still stronger liquor, and finally in neat extract 25° Bé. In these later liquors the rotation need not continue more than half the total time of immersion.

In another process, the goods are delimed and somewhat plumped with acetic acid. They are then taken through a series of suspenders ranging from 25—50° Bkr., which involves 10 to 14 days. The goods are then drummed in a 70—80° Bkr. extract liquor for twelve hours, and afterwards in neat extract, 200° Bkr. (25° Bé), for thirty-six hours.

In another method the goods are suspended after deliming in a weak (about ·3 per cent.) and slightly acid solution of formaldehyde for sixteen hours, and then placed directly into a 70° Bkr. extract liquor, finishing off as usual in liquors of gradually increasing strength.

Great difficulties have been experienced in many hands in obtaining a thorough and even tannage, the thicker parts of the hides being very liable to yield patches quite untanned. Prolonged drumming sometimes completes the tannage of these portions, but is apt to cause the rest of the hide to dry out hard and brittle. The essential conditions necessary for the successful drum tannage of heavy leather have not been as yet completely investigated, and where empirically discovered have not been fully made known.

CHAPTER XV

THE TANNAGE OF BELTING, HARNESS AND UPPER LEATHER, ETC.

The Tannage of Belting Leather is in many respects similar to the tannage of sole leather, so much so, indeed, that some manufacturers give the same tannage to sole and strap butts, and sort them before finishing. As a somewhat softer result is desired, however, greater quantities of gambier, myrobalans, etc., are usually employed. The layers also are generally not so strong as for sole leather on account of the nature of the finish. After scudding, the butts enter the **suspenders** (8—30° Bkr.), in which they remain two or three weeks. These liquors should not be too strongly acid, as a rather pliable leather is required, and excess of acid produces crackiness. The goods afterwards enter the **handlers** (30—45° Bkr.), in which they remain four weeks. As gambier tannages carry grease well, the butts are now given a **gambier round** (50—55° Bkr.), in which liquors they are suspended for 14 to 18 days, handling every day. Occasionally a little myrobalans or chestnut extract is used to make up the head liquor. The weak liquors are run to the handlers and worked down the yard. The goods now enter the layers, which are as follows:—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	50°	1	4 cwt. myrobalans.
2nd	55°	2	2 cwt. myrobalans and 2 cwt. mimosa bark.
3rd	60°	4	2 cwt. myrobalans and 2 cwt. valonia.
(4th)	70°	4	(for "heavies") 4 cwt. valonia.
(5th)	80°	4	(for "extra heavies") 4 cwt. valonia.

In making up the strong layer liquors some amount of chestnut and quebracho extract is employed.

German belting hides are given a six weeks' suspension

starting in a 7° Bkr. liquor. The liquor is changed twice a week for a slightly stronger infusion, the goods remaining in the same pit. They receive twelve liquors in all, the last being 24° Bkr. Occasionally the suspenders only run up to 14° Bkr., in which case a handler round is also given. The goods are now rounded and the butts are given two layers. In the first liquor (24° Bkr.) they are dusted down with 10 cwt. pine bark, 10 cwt. oak bark and 4½ cwt. valonia, and are allowed to lie six weeks. In the second liquor (28° Bkr.) they are dusted down with 11½ cwt. of oak bark, 5½ cwt. valonia, and 4½ cwt. pine bark, and remain in this eight to ten weeks. The leaches are made up from a blend of ⅔ pine bark, ⅙ quebracho and ⅙ myrobalans.

The Tannage of Harness Leather differs somewhat according to the quality of the goods and whether light or heavy harness is being made.

Light harness backs (high class) are entered into **suspenders** at 8° Bkr., and are handled forward every day for three weeks until they reach the head liquor (20° Bkr.). They then pass into the **handlers** (20—35° Bkr.) for six weeks, two of which are **dusters**, ½ cwt. myrobalans and ¼ cwt. oak bark being used for every 100 backs, and sufficient gambier to bring up the strength of the head liquor to 38° Bkr. The **layers** are as follows :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	35°	1	4 cwt. oak bark.
2nd	40°	2	4 cwt. oak bark and 1 cwt. myrobalans.
3rd	50°	3	3 cwt. oak bark and 1 cwt. extract.

The extract is found to counteract somewhat the influence of the myrobalans.

Heavy harness backs (high class) are put through **suspenders** in about the same time, but in rather stronger liquors (8—30° Bkr.), and next go into the **handlers** (30—40° Bkr.), a series of nine pits. In these they remain only a month, but they are given **a duster round** (40—45° Bkr.) of three pits, the goods being handled each day. The **layers** are now entered :—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	50°	2	4 cwt. oak bark.
2nd	55°	3	4 cwt. oak bark.
3rd	60°	4	4 cwt. oak bark.
4th	65°	4—6	4 cwt. oak bark and 1 cwt. valonia or mimosa.

A shorter method, with more tannin added as dust, is as follows:—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	50°	1	2 cwt. oak bark and 2 cwt. myrobalans.
2nd	55°	2	2 cwt. oak bark and 2 cwt. mimosa.
3rd	60°	3	2 cwt. oak bark and 2 cwt. valonia.
4th	65°	4 - 6	3 cwt. valonia and 1 cwt. myrobalans.

The fourth layers are only given when the tanner is not also the currier. The leach liquors are made from oak bark and myrobalans.

Cheap harness backs are given the following tannage:—

Having received an excess of boric acid they enter a 16° Bkr. **suspender** liquor and work up to 30° Bkr. in 14 to 18 days, and then enter the **handlers** (30—45° Bkr.) for one month. The head handler is an old layer liquor made up from 40—45° Bkr. with gambier, and in this pit the goods are dusted down with 1 cwt. myrobalans. The **layers** are as follows:—

Layer.	Bkr. strength.	Time in weeks.	Material, etc.
1st	64°	1	2 cwt. oak bark and 2 cwt. myrobalans.
2nd	51°	2	3 cwt. myrobalans, 1 cwt. mimosa bark, $\frac{1}{2}$ cask chestnut extract.
3rd	55°	3—4	2 cwt. myrobalans, 2 cwt. mimosa bark, $\frac{3}{4}$ cask chestnut extract.
4th	60°	4	1 cwt. myrobalans, 3 cwt. mimosa bark, $\frac{3}{4}$ cask chestnut extract.

The fourth layer is only given to the heavy goods, and the layer fishings are used for the leaches, together with some valonia and mimosa. If the tanner does not curry his own goods it is often profitable to give a fifth layer of 75° Bkr.

German harness hides are given a week in paddle after scudding, starting with a very weak liquor and gradually strengthening by the addition of oak bark and pine bark in equal quantities. The rest of the tannage is done in suspenders (7—21° Bkr.), in which the goods remain in the same pit all the time, the liquors being pumped over into the next pit. They remain three days in the first liquor and a week in each of the rest. The liquor for the suspenders is made up from six parts pine bark and two parts each of quebracho, myrobalans and mimosa bark.

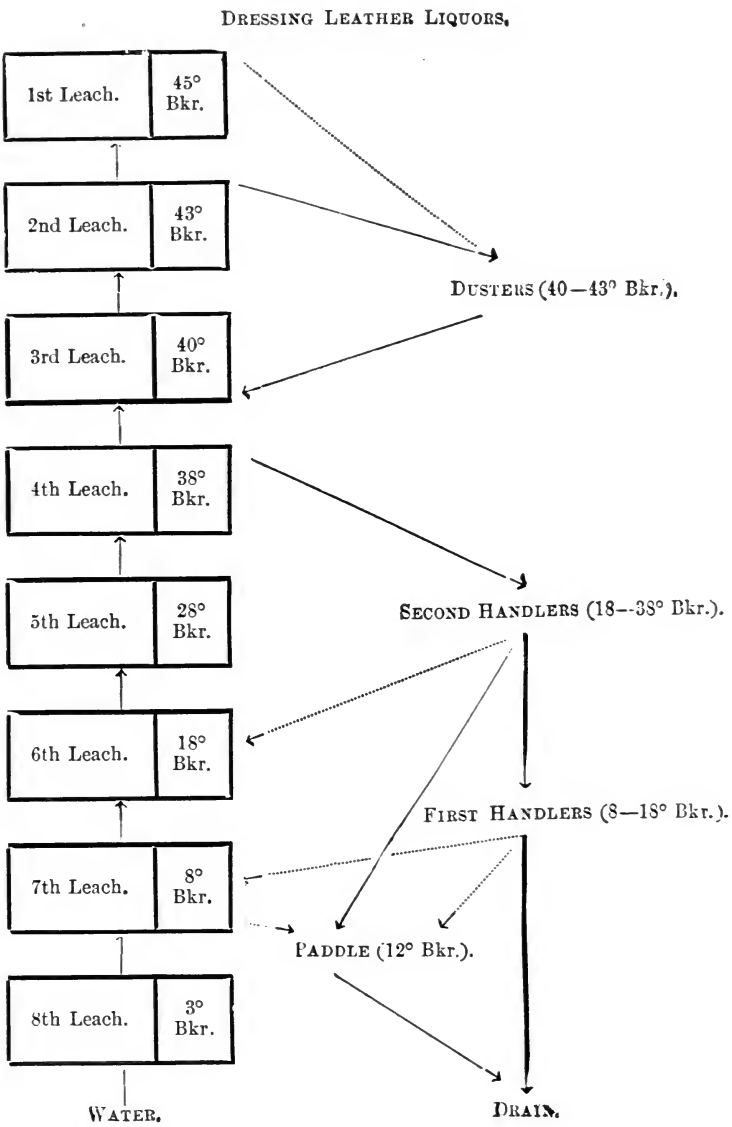
The Tannage of Dressing Hides for Upper Leather is largely carried out by oak bark and valonia, assisted by the liberal use of gambier and a moderate proportion of mimosa bark. The hides may be tanned whole, but are sometimes cut into sides and occasionally rounded. They are first coloured off in **paddle** in a 12° Bkr. liquor obtained from the second handlers or leaches. This liquor may be strengthened up again with gambier for a second or third pack, but is afterwards run away. The goods are paddled 2 to 5 hours, and then enter the **first handlers** (8—18° Bkr.) for a fortnight. These consist of a round of six pits, which receive a liquor each day from the second handlers, and a new pack on alternate days. A single shift is given, therefore, on the day no pack is received, and a double shift on alternate days when the green packs. The hides next pass through the **second handlers** (18—38° Bkr.), which are also rounds of six pits. They remain in these liquors for a month, a new pack entering the round every fourth day, and a new liquor being given on every other day. The goods are, therefore, given a single shift forward each day. The head liquors are obtained from the fourth leach, and the strength made up with about 2 cwt. of gambier. Any spare liquors are returned to the sixth leach. The goods now go into **dusters** (40—43° Bkr.) for six weeks. Rounds of six pits may be used, in the two most forward of which the goods are dusted down with 1 cwt.

mimosa bark. A little gambier may be used also in this round. The goods are then drawn, sumached and dried out.

In leaching for dressing leather, it is important to bear in mind that heavily bloomed goods are not desired, and it is, therefore, usual to leach slowly, so that the bloom deposits in the leaches. With this object it is customary not to use the head leach as a source of liquor for the yard, at any rate for a few days, and it is a common plan to return used liquors to the leaches, after passing them through a round, before working them down the yard. For the tannage described, a system of eight press leaches will be found convenient, the second leach being used as the source of the liquors, which after passing through the dusters are returned to the third leach. A suitable blend for leaching is ½ valonia, ¼ oak bark, ¼ mimosa bark. The liquors are worked down the yard as shown on opposite page.

The Tannage of Hides for Army and Navy Uppers is a soft mixed tannnage, in which gambier, myrobalans, valonia and a little oak bark are used. They are started ("grained") in **paddle**, which receives an old handler liquor and a bucket of strong gambier infusion for every dozen hides. The goods run in this liquor for one hour. Sometimes the graining is done in pits, the pack being handled three times and the liquors strengthened each time with one-third the above proportion of gambier. After draining for a short time they go to the **handlers**, a series of six pits of gradually increasing strength, and are finished off in five new leach liquors strengthened with gambier (2 lbs. per hide), and a single **layer** of one week, dusting down with valonia and mimosa bark. They are, therefore, not split until the tannage is complete. The offal is largely worked up for coloured boot uppers.

The Tannage of American "Split Hides" is chiefly with hemlock, but sometimes with pure gambier liquors. In the former case the sides after bating are suspended in the "handlers," which may be a series of fourteen pits, handling forward on alternate days, or a round of six or seven pits, remaining in each four days, so that in either case about a month is taken. The goods are tacked on laths or racks with copper nails, and handled very frequently in the early liquors,


Dressing Leather Liquors.
1st Leach.
45° Bkr.
2nd Leach.
43° Bkr.
Dusters (40—43° Bkr.).
3rd Leach.
40° Bkr.
4th Leach.
38° Bkr.
Second Handlers (18—38° Bkr.).
5th Leach.
28° Bkr.
6th Leach.
18° Bkr.
First Handlers (8—18° Bkr.).
7th Leach.
8° Bkr.
Paddle (12° Bkr.).
8th Leach.
3° Bkr.
Water.
Drain.

or are first coloured off in paddle. The strengths of the head liquors vary very considerably in different yards and with the different substance and destiny of the goods. The sides are now split and the grains re-tanned for several weeks in handlers or layaways, the liquors being hemlock bark leach liquors strengthened for the heavier goods with hemlock extract. The "heavy" splits receive a further few weeks tannage in hemlock liquors, the "medium" splits with hemlock, quebracho, gambier or sumach, and the "light" splits a short tannage with gambier and sumach. In the western yards the goods are often taken through the handlers and layaways before splitting.

The Tannage of Dressing Hides for Legging Leather is started by **suspending** the backs in mellow liquors for three weeks, handling frequently. The acidity of the liquors should be kept up by the addition of lactic acid, especially if the goods have not been delimed completely. The packs now pass through a round of **dusters**, which takes six weeks, handling occasionally. The strength of the liquors is increased gradually with extract, and the goods dusted down with increasing quantities of oak bark. They then pass into the **layers** for four to six weeks, which contain liquors a few degrees stronger. The fresh liquors are made up with quebracho and gambier.

The Tannage of E. I. Kips differs considerably in different yards, but gambier is the mainstay of most of the processes, assisted by valonia, oak bark and myrobalans. In one process the goods are first **paddled** in a 10° Bkr. liquor made from oak bark and myrobalans, which colours them and draws the grain somewhat. After remaining in this for about three hours they go into the **first handlers**, a round of four pits (4—20° Bkr.), thus receiving at first a liquor weaker than that in the paddle. They are handled every day and sent forward every alternate day. The goods now go through the **second handlers** (20—45° Bkr.) for six weeks. The liquors are made up from a blend of $\frac{1}{3}$ oak bark, $\frac{1}{3}$ myrobalans and $\frac{1}{3}$ valonia, the leaching of which must be done slowly in order to allow the bloom to deposit. The leach liquor is brought up to 45° Bkr. with gambier in the form of a hot concentrated infusion made in a special leach pit.

In another process only valonia and bark are leached and the liquors made up with gambier. The goods receive, after paddling, three weeks in the **first handlers** (3—20° Bkr.) and three weeks in the **second handlers** (20—30° Bkr.).

In both these processes the goods are given three or four new liquors towards the end, and are then finished off in a strong liquor (no dust used) in which they remain 4 to 7 days according to their substance.

Another process is used in which the goods remain in the handlers for less time (four weeks for the lighter and six weeks for the heavier kips) and are given layers of one or two weeks. This saves labour and gives better weight and colour. The layer is made by sprinkling the bottom of the pit with oak bark and placing the kips into the pit one by one, grain to grain and flesh to flesh, putting between the grains a paste made from myrobalans, valonia, sumach and gambier, and between the fleshes a paste made from sumach and gambier only. The pit is now filled with the best liquor from the leaches.

A little mimosa bark is often added to the leaches and to the grain paste for the layers. The time of paddling varies in different yards from half an hour to five hours, according to the strength of the liquor and the condition and destiny of the goods.

The Tannage of Heavy Calf is commenced by paddling in a sweet oak bark liquor (8° Bkr.) with perhaps a little sumach. They then enter the **first handlers** (6—24° Bkr.), in which they are moved forward each day for four weeks. They afterwards go through a series of **second handlers** (24—40° Bkr.) for four to six weeks. The head liquors are made up from $\frac{1}{3}$ oak bark, $\frac{1}{3}$ myrobalans and $\frac{1}{3}$ gambier, the myrobalans being sometimes partially substituted by valonia.

The Tannage of "Shoe Calf" is also with oak bark and gambier. The goods go through the **first handlers** (8—16° Bkr.) in about a fortnight, the head liquor being made up from the weakest second handler liquor by means of gambier and perhaps a little sumach. They now enter the **second handlers** (16—20° Bkr.) in which they remain 16 days, bark only being used to make up these liquors. The "heavies" receive a layer (22° Bkr.) of two weeks, using 2 to 3 cwt. of bark.

Another process is employed in which only **paddles** or **paddle-pits** are used. The skins are commenced in a 5° Bkr. gambier liquor, which is acidified with acetic acid (1 pint to 60 skins). When coloured off they are horsed up overnight and put then into a 10° Bkr. liquor for five hours, and again horsed up two to three hours. They are then paddled in a liquor 5° stronger still and horsed up, this being repeated until the goods are struck through. A 20° or 25° Bkr. liquor usually accomplishes this. They are now paddled in a 25° Bkr. liquor, to which 2 gallons of oakwood extract have been added per 60 skins, horsed up occasionally, and the paddle liquor strengthened gradually by the addition of extract until it is 35° Bkr. The time taken in the later paddle liquors naturally depends upon the substance of the skins.

The Tannage of Hides for Bag, Portmanteau and Bridle Work, etc.—Flat, evenly-grown cowhides are chosen for this work. They are limed and bated like ordinary dressing hides. They are drummed in water at 20° C., then in boric acid solution (using 1 lb. boric acid to each 3—4 hides) and then enter the tan liquors. If a grain is required (as for bag hides), the goods have a **colouring round** of two pits side by side and of the same strength (12° Bkr.). These pits contain new liquors from the leaches together with a little oak bark or myrobalans, according to the tint required. The hides are thrown one by one into one pit and immediately hauled and thrown into the next, and so on; being changed in all six times in a period of four to five hours. They then enter the **first handlers** (8—20° Bkr.) for about a fortnight. The head liquor is a 16° Bkr. liquor from the second handlers made up to 20° Bkr. with gambier. Goods for bag work are split at this stage, being plump and coloured through, but for the heavier portmanteau work go straight forward. Both classes now pass into the **second handlers** (20—40° Bkr.) for about a month, the goods being handled each day. The head liquors are from the leaches in which oak bark, myrobalans, and a little mimosa and valonia are used. A 35° Bkr. liquor is obtained, which is made up to 40° Bkr. with quebracho extract. No gambier is used in this round. The bag hides are now completely tanned, but those for portmanteau and

bridle work receive two **layers** of 40° Bkr. liquors, dusting down with oak bark. The packs remain fourteen days in each layer. The splits are finished by a cheap drum tannage with extracts.

A cheaper tannage may be carried out by graining in **paddle**, the liquor being made of chestnut extract, quebracho extract and myrobalans in about equal proportions. They then pass through a **handler** round of four pits (11—20° Bkr.), in each of which they remain one day, the liquors having a fair acidity. The goods are now plump and may be split. They are then finished off by drumming in a mixture of chestnut and quebracho extracts (2 : 1), gradually strengthening up the liquor from 30—50° Bkr. The splits receive the old drum liquors, strengthened where necessary with quebracho extract.

A still cheaper method is used in which the goods are given a short liming with the help of sulphide, bated with acids in paddle or latticed drum, and worked out of the beam house through tepid water. They are then drum tanned for three days, gradually strengthening the liquor, split and finished in stronger liquors of myrobalans and chestnut or quebracho extract.

The Tannage of Picking Band Butts is a slow oak bark treatment in weak liquors. The butts are five to six weeks in the **first handlers**, being hauled very frequently, especially in the early stages. In the **second handlers** they are hauled only once a month, and in the **layers** once in three weeks to receive new liquors. The whole tannage lasts at least six months.

CHAPTER XVI

THE TANNAGE OF MOROCCOS AND LIGHT LEATHERS

The Tannage of Goat Skins by the vegetable tanning materials, chiefly sumach, yields after dyeing the true morocco leather, of which a great many varieties are manufactured, according to the class of goods for which they are intended.

For high-class work, soft leathers, and fine grain finishes, the bottle (or bag) tannage is used. Each pelt is sewn up all round to form a bag, having the grain side outward and leaving a small opening at the hind shank. The stitching is done by machine or by hand labour, and is afterwards tested by filling the bag with water. A strong infusion of leaf sumach is now made, and the bags nearly filled with this by means of a funnel, and then inflated with air and the hole tied up. The bags in this distended condition are now thrown into a large vat containing a warm, weak sumach liquor, in which they float. They are then kept in constant motion by stirring and pushing into the liquor with poles. After some hours' immersion they are piled on a rack above the vat to drain, and the liquor inside the bags is thereby pressed out by its own weight and the pressure of the piled skins. Occasionally mechanical pressure is also employed. The bags are again filled and the process again gone through, immersing the skins now in a stronger sumach liquor. The stitching is now undone, and the goods washed in paddle and struck out by machine or by hand and dried. By this process the skins are quite effectively tanned in twenty-four hours or less, and a very soft and fine leather results, which, however, is rather open and porous.

For common skins and bolder grains a tannage in paddle is used. A three-paddle system is employed in which a fresh sumach liquor is made up for each pack, and each liquor is used three times. The goods first enter a mellow liquor

through which two packs have already passed, afterwards into a liquor which has been used once, and then into a new, fresh

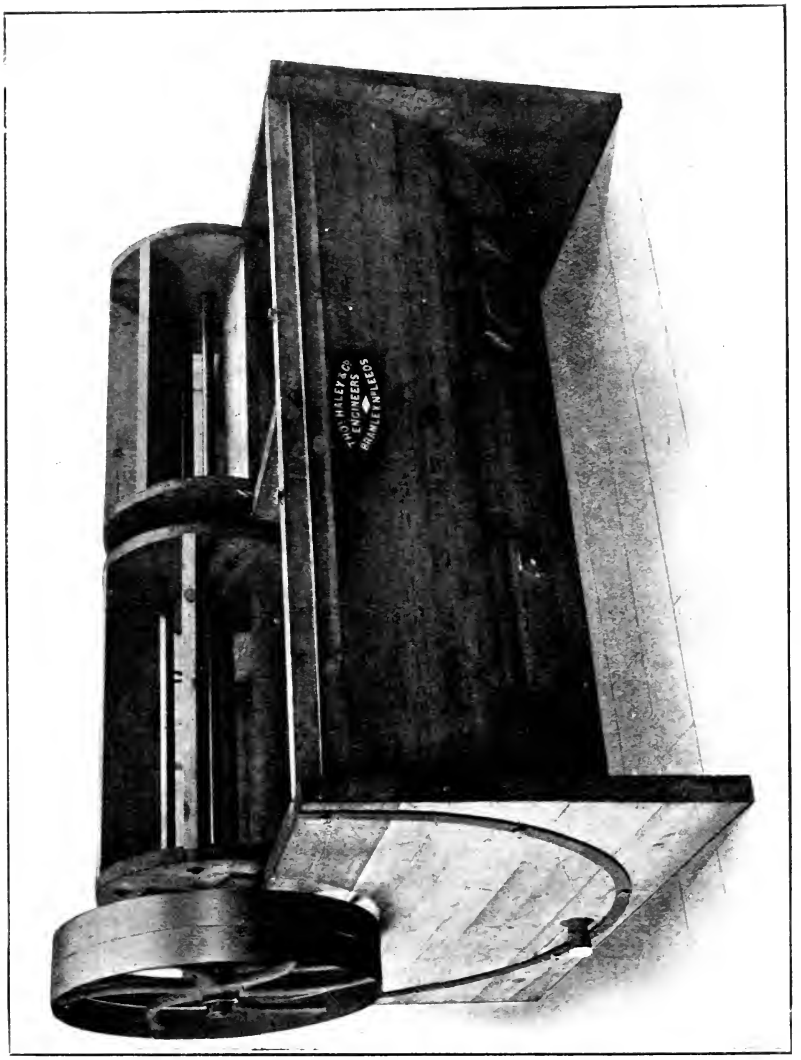


FIG. 58.—Double paddle for light leather tanning.

liquor of good strength. Two or three bags of sumach should be used for every twenty dozen skins, and the temperature of

the paddle liquors should be about 27° C. The whole tannages last about a fortnight.

For firmer leathers another method is also employed in which a handler round is given, and a blend of oak bark and sumach is employed. The skins are first paddled in an old sumach liquor, or a weak mellow bark and sumach liquor, to give good colour. In the latter case a 10° Bkr. bark liquor is used, with one bag of sumach for every twenty dozen skins. Much of the earlier handling may be substituted, and a shorter tannage thereby obtained, by paddling, or by drumming in latticed drums. Oak bark gives a much "faster" tannage than sumach, and will dye equally well for dark colours.

The Tannage of Seal Skins gives a special class of morocco leather with a characteristic grain.

For bookbinding work the small skins are chiefly used, and are often tanned with sumach only according to the specifications of the Committee of the Society of Arts. The paddle method described for goat skins may be used.

For fancy work heavier skins are employed, and are tanned with sumach and oak bark. The drenched skins are paddled for three days in mellow sumach liquors of gradually increasing strength until coloured through. They are now split, and the grains go into the handlers (8—24° Bkr.) for three weeks, handling each day for the first 10 days, and on alternate days for the rest of the time. The head handler is obtained from the leaches in which oak bark is the principal material, though a little mimosa bark or myrobalans is sometimes used. The goods are now given 2 days in a fresh sumach liquor to improve the colour. The fleshes are finished by drumming for several days in extract liquors, which are gradually strengthened. They are afterwards japanned.

Seal skins are now often split in the limed state by the alternating knife machine, and the grains given a shorter tannage with oak bark and sumach. The goods are "grained" in paddle by a used bark and sumach liquor for several hours, and then pass into the handlers for 10 days, in which oak bark liquors alone are used. They are then finished off by

paddling in a liquor made up of oak bark and sumach, with perhaps a little oakwood extract. The splits are coloured off in mellow bark liquors and finished as above.

Another tannage is with gambier and oakwood extract. The goods go through the first handlers (10—15° Bkr.), in which gambier only is used, and in which the goods are well struck through. The goods are handled very frequently in the early stages. They next enter the second handlers (15—20° Bkr.), which are made up from oakwood extract and some gambier, and are finished off in a bath of sumach liquor to give good colour.

For enamels and boot work the heavy skins are used, and often receive a tannage of several weeks in oak bark liquors, with perhaps a small proportion of extract, mimosa bark, or gambier.

The Tannage of Calf Skins also varies somewhat, according to the purpose to which they are to be put.

For bookbinding work the skins are often given the bag tannage. The skins are paired according to size, and the pairs are sewn together grain outwards and filled with sumach infusion. They are then placed in a pit containing a used sumach liquor until next day, refilled and returned, and on the third day drained overnight on the shelf. They are now cut open, worked over the beam on the flesh side, and returned to the pit until the seventh or eighth day, handling each day. The tannage is now complete.

Many people, however, use the paddle for the tannage of calf for bookbinding. The method is somewhat similar to that used for goat skins; the goods are started in a used sumach liquor, and finished off in fresh sumach, and occasionally a sumach layer is given. Warm liquors (20—22° C.) are used in the paddles.

For fancy work the skins are struck through with sumach and then paddled in oak bark, myrobalans, or chestnut extract liquors. Sometimes only sumach, or sumach and oak bark, are used.

For light upper work they are started in sumach liquors, put through a round of handlers for 10 days, and finished by rinsing through a clear, weak sumach liquor.

The Tannage of Sheep Skins differs very considerably with different classes of goods.

For basils the skins are tanned in many ways. Scotch basils are first paddled in an 8° Bkr. larch bark liquor, and gradually given stronger liquors until struck through, which is usually in about 2 days. They are then horsed to drain, and degreased by hydraulic pressure. After soaking, they are retanned for several days in stronger bark liquors (11—20° Bkr.). The first liquors should be of fair acidity.

In the West of England the skins are often given an oak bark tannage in pits, starting and finishing by paddling in sumach liquors. An increasingly common method is to use the paddles throughout. The liquors are made from oak bark, myrobalans, and gambier, and sometimes the oak bark is replaced by extracts. The skins are first paddled for half an hour in a nearly exhausted liquor, drained, and then run in a stronger bark liquor, which is strengthened with gambier at the end of one, three, and six hours respectively. They are then drained in pile overnight, degreased by pressure, and finished off in paddles with stronger liquors, the whole tannage being accomplished within a week.

In America a blend of two-thirds quebracho and one-third hemlock is often used for tanning basils, though hemlock alone is used, and drum tannages in palmetto extract and paddle tannages in oak bark and other extracts are also common.

For skivers the skins are given a sumach tannage, partly in paddle, commencing with 2 days in mellow liquors, and finishing up with fresh sumach infusions. The liquors are warmed up as the tanning proceeds, and considerable care is taken in handling the goods, as their light substance and small strength of fibre causes them to tear easily. American skivers are tanned with sumach, and also with hemlock, and blends of this with quebracho. In the latter case bleaching is often necessary.

For roans a rather long sumach tannage is given. The skins are tanned in pits, but are finished off in paddle.

For roller leather a smooth grain is required, and a long oak bark tannage is given in weak liquors. It is now usual to

replace the oak bark to some extent by oakwood extract and other materials. The goods are first coloured through in paddle, three liquors of slightly increasing strength being usually sufficient. They are then degreased by hydraulic pressure, paddled in warm water to soften and remove sawdust, and then drummed in fairly hot water until all press creases disappear. Sometimes they are placed in fairly hot water in a pit and left overnight, and occasionally weak liquor is used. The skins are now tanned out in suspenders, eight or ten liquors being given over a period of 18 to 20 days.

CHAPTER XVII

THE TANNAGE OF CHROME LEATHER

THE mineral tannages, *i.e.*, the manufacture of leather by the action on pelt of mineral salts, have in recent years developed to such an enormous extent that the permanency of many of the time-honoured vegetable processes is now a matter of considerable doubt. Although the alum-dressed ("tawed") leathers have been known for some centuries, and have represented the possibility of mineral tannages, their commercial importance is now small when compared with the more recently introduced "chrome leather," and hence in this volume the latter is dealt with first and to a somewhat fuller extent.

The action of chromium salts, normal and basic, on hide substance was first studied by Knapp,[1] who concluded that their action could not be made of any practical value, and turned his attention to the action of iron salts. Somewhat later Cavallin, whose object was dyeing rather than tanning, took out a patent for treating skins first with potassium dichromate, which was afterwards reduced with ferrous sulphate; but the process did not produce a satisfactory article. Heinzerling, in 1879, patented a process for making chrome leather in which the skins were treated with alum and potassium dichromate, the latter being reduced at the expense of the hide fibre and the fats employed in currying. This process also, however, did not prove a commercial success. In 1881 Eitner obtained Austrian patents for a combined chrome and fat tannage, recommending the use of the "normal basic salt" Cr (OH) SO_4, obtained by adding soda to a chrome alum solution; but he also found difficulties in finishing his product into a satisfactory article. In 1884,

[1] "Die Natur und Wesen der Gerberei," 1858.

however, an important advance was made in the patenting of the so-called "two-bath process" by Augustus Schultz. In this process the skins were treated first with a solution of chromic acid made by the action of hydrochloric acid on potassium dichromate, and afterwards with a solution of sodium thiosulphate[1] and acid, thereby causing the reduction of the chromic acid to a basic chromic salt, which produced the tannage. This process proved commercially successful in the manufacture of light leathers, and although some little variations from the proportions and nature of the materials specified in the original patent are now often admitted, the process may still be used to give a satisfactory leather. In 1893 Martin Dennis revived and patented the original process of Knapp, which involved the use of a basic chromic chloride, and offered for sale a solution of such a salt.[2] This salt was used first in dilute solution, which was afterwards strengthened as the tannage proceeded. This "one-bath process" was also found to produce excellent leather, and soon became popular for the manufacture of chrome calf and of the heavier chrome leathers. The validity of the patent has always been a matter of doubt, and at all events cannot cover the use of basic chrome sulphates, which in practice are equally satisfactory. In 1897 Professor Procter published his one-bath liquor prepared by reducing potassium dichromate with sugar (glucose) in the presence of a limited quantity of hydrochloric acid, and since then many other modifications of these various methods have been applied with varying success.

The nature of the mineral tannages has been the subject of much discussion and research; but it is becoming increasingly recognised that there is a considerable resemblance in fundamental principle to the vegetable tannages. For the production of a permanent leather "it is not only necessary to dry the fibres in a separate and non-adherent condition, but so to coat them or alter their chemical character that they are no longer capable of being swelled or rendered sticky by water."[3]

[1] Often called "hyposulphite of soda," or "hypo."
[2] "Tanolin."
[3] Procter, "Principles of Leather Manufacture," p. 184.

In the vegetable tannages the astringent tannins, presented to the hide fibres in colloidal solution, are adsorbed by them and cause the contraction and separation of the fibres which is the first requisite for leather production. The colloids thus precipitated then undergo a further change in their chemical character, the nature of which is not yet completely understood, but which may involve oxidation, dehydration or polymerisation, and which at any rate is irreversible, giving rise to a product that will not swell or dissolve in water. Many mineral salts,[1] especially when used in conjunction with a certain amount of free acid,[2] will also fulfil the first condition necessary for the production of leather, viz., the isolation and dehydration of the fibres,[3] but will not permanently fix themselves in the fibres and cause these to lose their capacity for absorbing water. This second condition can be realised, however, when the salts yield solutions in which hydrolysis has taken place into free acid and colloidally dissolved basic salt or hydrate.[4] When such solutions are presented to skin, the free acid quickly penetrates and is adsorbed, but reversibly, *i.e.*, it can be removed by washing or neutralisation, whereas the colloidal basic salt penetrates more slowly but is adsorbed irreversibly. Such solutions are obtained from the salts of trivalent iron, chromium and aluminium. The normal salts of these metals are all hydrolysed more or less in this way, but unless made "basic" by the neutralisation of some of the free acid they are only to a very small extent capable of this permanent fixation. This is well illustrated in the long-known alum tannage (p. 239), in which the leather is easily wetted back and much of the alum removed by washing. When made basic, however, the salts of all these metals are capable of making leather, though its quality is much influenced by the nature of the acid radicle

[1] Such as ammonium sulphate.
[2] Such as the use of salt and acid in "pickling."
[3] Hence their usefulness in assisting the vegetable tannages.
[4] Any metal which forms an insoluble oxide is capable of producing a leather by the precipitation of that oxide within the skin and subsequent drying of the pelt. The fibres are then coated with the insoluble oxide, which prevents their being wet back. How far this tannage is analogous to an ordinary one-bath chrome tannage is open to dispute.

and the degree of basicity. With the common salts of chromium there is a much wider range of basicity permitting the production of a satisfactory leather, than in the cases of the salts of aluminium and iron, and this fact accounts to a large extent for the commercial success which has attended the use of the former. In the one-bath process the tannage is simple and direct; in the two-bath process it is more complicated in that the basic chrome salt is produced within the fibres.

The two-bath process involves, as signified in the name, the treatment of the hides or skins in two distinct solutions, generally spoken of as the "chromic acid bath" and the "hypo bath."

The former consists usually of a solution of potassium dichromate to which hydrochloric acid has been added and free chromic acid liberated, as follows:—

$$\underset{294}{K_2Cr_2O_7} + \underset{73}{2\,HCl} = \underset{149}{2\,KCl} + \underset{200}{2\,CrO_3} + \underset{18}{H_2O}$$

In the original Schultz bath 5 per cent. of potassium dichromate and $2\frac{1}{2}$ per cent. of concentrated hydrochloric acid (or $1\frac{1}{2}$ per cent. of sulphuric acid) were used on the weight of the pelt prepared for tannage. According to the equation, however, 294 parts by weight of potassium dichromate require 73 parts by weight of hydrochloric acid, and as the latter is sold commercially in a solution of about 30 per cent. strength (S.G. 1·16), 73 parts of HCl are obtained in about 250 parts by weight of commercial hydrochloric acid, and hence 5 per cent. of the dichromate would require $4\frac{1}{4}$ per cent. of hydrochloric acid for the complete liberation of the chromic acid.[1] In the Schultz bath, therefore, there is a considerable quantity of potassium dichromate undecomposed, and this has been considered useful both in preventing accidental overdoses of the hydrochloric acid, and in modifying the influence of the free chromic acid on the pelt. Eitner, however, prefers not only to liberate the whole of the chromic acid, but to use also a distinct excess of hydrochloric acid,[2]

[1] Similarly, 6 and 4 per cent. of dichromate will require 5·1 and 3·4 per cent. respectively of hydrochloric acid.

[2] Eitner suggests 4 per cent. dichromate and 4 per cent. acid.

as this actually gives better results, owing to the hardening and contracting influence of the chromic acid being counteracted by the tendency of the hydrochloric acid to swell the skins. With any great amount of acid, however, a quantity of common salt should be added to restrict the swelling action of the free hydrochloric acid. A further advantage of this acid bath is that it can be safely exhausted by a second pack of skins, which procedure is impossible in baths containing excess of unacidified potassium dichromate. Another modification of this bath which is often met with is the addition of aluminium[1] sulphate to the extent of 3 to 5 per cent. of the pelt weight. If this be done in the Schultz bath with excess of undecomposed dichromate, its effect is to liberate more chromic acid, becoming itself basic. It is difficult, however, to see where the advantage lies, as it is found to cause a decreased absorption of chrome, and yet to be largely washed out itself. If the acid chroming bath is employed the aluminium salt is quite useless, and no aluminium is found in the leather produced.

A further important point is the condition of the goods on entering this bath. So far it has been assumed that they have been in a neutral or slightly acid condition, direct from the deliming process, but it is also very common to pickle the goods previous to chrome tannage. This is an advantage, in that it affords some facilities for sorting the goods previous to tannage, and is supposed to produce a fuller and plumper product. In this case there are various methods of procedure, of which the most obvious perhaps is to depickle, and then proceed as usual. The depickling is generally brought about in a warm salt solution to which an excess of whitening has been added, or by means of a basic alum solution. Occasionally it is also done by a solution of "C.T. bate," to which alkali has been added. Where goods are received in the pickled state, depickling may possibly be the wisest plan, but if the pickling is done by the tanner the possibility may be considered of omitting this operation. The composition of the pickle will then have to be considered relative to its influence on the

[1] $Al_2(SO_4)_3$ 18 H_2O has mol. wt. 666, and K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O has mol. wt. 948.

composition of the first-bath liquor, and the simplest and most economical plan is to arrange that the acid on the pickled skins should be just the amount necessary for the liberation of the required amount of chromic acid in the chroming bath. A pickle of common salt and hydrochloric acid only is perhaps preferable in this case, a little salt being also added to the dichromate bath instead of hydrochloric acid; but a pickle of salt, aluminium sulphate and sulphuric acid is also often used in a similar way. Occasionally the acid is omitted from the second pickle and the goods merely "tawed" in alum and salt. This treatment is said to assist in preventing drawn grain, but in this case the chroming bath must be acidified. In no case should pickled goods be put into the acid chroming bath, at any rate without a very liberal addition of salt. Another method which has been successfully used is to place the goods in an acid and salt pickle, and gradually to add the bichromate to the same bath.

The chromic acid penetrates through the goods quickly and evenly, owing to its non-tanning nature, but it is essential for good results that motion should be given, and hence paddles or drums are employed, the former usually for light goods and where smooth grain is important, and the latter for heavier hides and where grain is less important. The concentration of the liquor has little influence on the absorption, the same amount of chrome being taken up eventually from weak as from strong solutions. In concentrated solutions the absorption is somewhat quicker, but it is important that there should be sufficient liquor for the goods to be moved freely, or drawn grain will result. Small variations in the ratio of dichromate to pelt have also little influence on the result. It will be clear that sulphuric acid, sodium bisulphate and other acids and acid salts (not organic) may be substituted for the hydrochloric acid; but these are not often employed. Similarly, sodium dichromate or chromic acid itself may be used in place of the potassium salt[1]. The absorption of chrome is in all cases lowered by the presence of electrolytes

[1] $K_2Cr_2O_7$ has mol. wt. 294, $NaCr_2O_7$, 2 H_2O has mol. wt. 298, and 2 CrO_3 has equiv. wt. 200, but is deliquescent. Hence, in practice, for potassium dichromate an equal weight of the sodium salt, or rather less of the free acid, may be substituted.

in the chroming bath, but this influence seems to depend almost entirely on the nature of the anions. Sodium chloride, nitrate or acetate, all bring down the percentage absorption of chrome, but the effect is much greater when sodium sulphate is used. Comparative experiments with sodium, potassium and ammonium sulphates have also shown that this decreased absorption is not influenced by the nature of the cations, but apparently due to the divalent anion SO_4''. The percentage absorption of chrome is increased in the Schultz bath as the proportion of hydrochloric acid is increased, and reaches a maximum approximately when the dichromate and acid are stoichiometrically equivalent and all chrome is present as free chromic acid. The chroming should be continued until the goods are "struck through" in the thickest parts (shown by cutting) with the yellow chromic acid, and after some further motion to ensure evenness, the goods are removed from the bath and horsed up or piled to drain. It has been found that if the skins are placed in a weak or neutral hypo bath there is a tendency to lose chromic acid by diffusion, which acid, though reduced by the thiosulphate, is not fixed in the skins, thereby causing both a waste and an undertannage. This tendency to "bleed," as it is termed, is lessened by allowing the goods to lie for some time (generally overnight) before the reduction is proceeded with, possibly by reduction at the expense of the pelt; but the goods should be carefully covered so that the action of light cannot cause this to take place to any great extent.

The second bath of the process consists of a solution of sodium thiosulphate, acidified with hydrochloric acid, the sulphurous acid thereby liberated acting as the reducing agent. Motion must be given in this case also, either in drum or paddle, the latter being generally preferred. The reactions in this bath are somewhat complicated, but according to Eitner, who studied the effect of gradually adding the acid, the course of the changes is represented in the following equations. With very little acid present the skins become brownish from the reduction of chromic acid to chromium dioxide, thus:—

(1) $3\ CrO_3 + 6\ HCl + 6\ Na_2S_2C_3 = 3\ CrO_2 + 6\ NaCl + 3\ Na_2S_4O_6 + 3\ H_2O.$

It will be noticed that sodium tetrathionate is formed, but that no sulphur dioxide is liberated or sulphur deposited. With more hydrochloric acid the skins brighten in colour, the reduction of chromic acid is to chromic chloride and more tetrathionate is formed. The reaction is as follows:—

(2) $2\ CrO_3 + 12\ HCl + 6\ Na_2S_2O_3 = 2\ CrCl_3 + 6\ NaCl + 3\ Na_2S_4O_6 + 6\ H_2O.$

With still more hydrochloric acid sulphur is deposited both in the bath and in the skins, the reaction being:—

(3) $2\ CrO_3 + 6\ HCl + 3\ Na_2S_2O_3 = 2\ CrCl_3 + 3\ Na_2SO_4 + 3\ S + 3\ H_2O.$

The reduction is now complete and the free hydrochloric acid consumed, but the excess of thiosulphate, which should always be present, causes further reactions, in which the chromic salts are made basic and a further quantity of sulphur deposited in the skins. These changes may be represented thus:—

(4) $Cr_2\ (SO_4)_3 + Na_2S_2O_3 + H_2O = 2\ Cr(OH)SO_4 + SO_2 + S + Na_2SO_4.$

(5) $2\ CrCl_3 + Na_2S_2O_3 + H_2O = 2\ Cr(OH)Cl_2 + SO_2 + S + 2\ NaCl.$

In actual practice these changes were by no means thought to be in such definite steps, but to a large extent are taking place simultaneously, according to the conditions under which the second bath is applied. The reactions of the second bath have been studied more recently by Stiasny, who investigated the conditions which determine the amount of sulphur deposited. He proved that under certain conditions a reaction took place between the dichromate acid and thiosulphate, in which tetrathionate was formed along with a basic chromium salt, and no sulphur was deposited.

(*a*) $3\ K_2Cr_2O_7 + 16\ HCl + 4\ Na_2S_2O_3 = 6\ KCl + 6\ NaCl + Na_2S_4O_6 + 4\ Cr(OH)SO_4 + 2\ Cr(OH)Cl_2 + 5\ H_2O.$

In the ordinary hypo bath, however, another reaction takes place alongside it involving the precipitation of sulphur.

(*b*) $K_2Cr_2O_7 + 6\ HCl + 3\ Na_2S_2O_3 = 2\ KCl + 4\ NaCl + Na_2SO_4 + 2\ Cr(OH)SO_4 + 2\ H_2O + 3\ S.$

These reactions do not take place in any fixed proportion, the extent of each varying with the conditions of the reducing bath. It is clear also that the amount of sulphur deposited depends on the same conditions.

It has also been shown that whether hydrochloric or sulphuric acid is used in the two-bath process the tanning agent is basic chromium sulphate, and that well-washed two-bath chrome leathers contain sulphates and no chlorides. Hence another equation must be given to show completely the changes of the second bath.

(*c*) $Cr(OH)Cl_2 + Na_2SO_4 = Cr(OH)SO_4 + 2\ NaCl.$

In consequence of the rather complicated changes in the hypo bath the best practical mode of procedure is therefore only to be determined from empirical observations, but it is probably best in all cases to insert the goods in the hypo and then to add the acid slowly. If added quickly, the rate of the reduction is increased, but much sulphur dioxide escapes to the air, and much thiosulphate and hydrochloric acid is therefore wasted. There is also a liability to form too acid chrome salts and consequently to cause an under-tannage. Where the acid chroming bath has been used no addition of hydrochloric acid should be made to the hypo bath for some time, and then a diluted solution should be added in successive portions. It is nevertheless customary in many factories to add all the acid to the hypo bath and to insert the goods quickly when sulphur begins to be precipitated. The ordinary colour changes are from yellow to olive-brown, green, and finally to a uniform blue throughout their substance, and when this has been accomplished the tannage may be considered complete, but it is always advisable to stop the motion but leave the goods for some hours, preferably overnight, in the excess of undecomposed thiosulphate. This not only ensures complete reduction and deposition of the basic chrome salt, but also permits the thiosulphate to act as a "neutralising" agent (p. 355) in virtue of its weakly alkaline

character. Occasionally a fresh bath of thiosulphate without acid is used for this purpose, and it will be seen at any rate that an excess of thiosulphate is always an essential for this bath.

The concentration of the bath is also a matter of rather more importance than in the case of the chroming bath, and greater dilution is desirable to prevent the loss of sulphur dioxide to the air. For the same reason also the temperature should be kept low. The exact quantity taken varies in different works from 10 to 20 per cent. of the pelt weight, according to the mode of application and nature of the goods. In the original Schultz bath the quantities specified were 10 per cent. thiosulphate and 5 per cent. hydrochloric acid, and if the acid is added gradually and the solution dilute, this is quite sufficient for light goods, but where the acid is added quickly, and in the case of heavier skins and hides, it is desirable to use from 12 to 15 per cent., and even more, of thiosulphate, with sufficient acid to complete thoroughly the colour changes mentioned above. This can generally be accomplished by a weight of acid about half the weight of the thiosulphate used, but is somewhat less when the acid chroming bath is employed. It is often usual to employ as a preliminary "dip" a solution of thiosulphate (occasionally acidified if the acid chroming bath has not been used) through which the goods are drawn and then piled or horsed to drain. The advantage of this procedure is in both preventing "bleeding" and drawn grain. If the former is chiefly feared a somewhat strong solution is used, if the latter, a weak solution is desirable. The goods are subsequently reduced in a hypo bath of ordinary strength.

Many substitutes for sodium thiosulphate have been suggested or patented for use in this bath, including sulphuretted hydrogen, acidified sulphides and polysulphides, sulphites, bisulphites, hydrogen peroxide, nitrous acid, lactic acid, etc.; but none are so easy to manipulate or so satisfactory as the thiosulphate.

The one-bath process bears some resemblance to the vegetable tannages, not only in its fundamental basis, but also in the principles of its practical application. In the first place the

results differ considerably according to the basicity of the salt employed, and this effect of basicity was considered analogous to the varying astringency of the vegetable tannins. The more acid salts penetrate rapidly and evenly through the goods without drawing the grain, and also swell considerably; but a very light tannage is given and much of the chrome salt will wash out again. The more basic salts on the other hand tan more slowly, the acid portion of the hydrolysed salt rapidly colouring through as before, but the full tannage proceeding slowly from the surface. The tannage in this case, however, is both heavier and more permanent. If very basic salts are employed the surface of the pelt becomes overtanned, an even more basic salt being deposited, and only a more acid salt penetrates into the interior. The tannage, therefore, is uneven, and the resulting leather has a brittle or tender grain. The very basic salts, like the astringent tannins, have also the effect of drawing the grain. The degree to which the salts of chromium should be made basic in order to produce the fairly quickly penetrating, even and irreversible tannage varies with the nature of the acid radicle. In the case of chrome alum, which is one of the commonest salts used for this process, the best results are obtained by adding sufficient soda to form the so-called "normal basic salt" $Cr(OH)SO_4$, but in the case of chromic chloride the basicity must be made distinctly greater to produce the same results, the salt $Cr_2Cl_3(OH)_3$ in which half the acid has been neutralised being found satisfactory for many purposes. It will be readily understood, therefore, that the addition of common salt to a sulphate liquor has the effect of reducing the apparent basicity of the solution and of causing a decreased absorption of chrome, and that similar effects, one way or the other, will be caused by the presence of other neutral salts. In the cases of tartrates and lactates this apparent reduction in basicity has been found to be specially marked. The influence on basicity of the condition of the green goods is also a point to be considered. It is generally considered best to have the pelt in a neutral or slightly acid condition; but when a somewhat firm result is desired the deliming need only be on the surface, and a more basic tannage will then be obtained without any danger to the

grain. It is common also for the prevention of drawn grain to use a bath of alum, or of alum and salt, and in some cases flour is also employed and the goods dried out and "aged" as in tawing (p. 240). If incompletely delimed goods are placed in such a bath a slight basic alum tannage will be given. Pickling is also often practised, but it is perhaps most usual in this case to depickle in order to give the alum and salt treatment. They may be depickled with salt and whitening, salt and soda, alkaline C.T. bate, or basic alum salts. Goods may also be tanned without depickling, in which latter case the effect of the pickling acid in reducing the basicity of the solution will have to be annulled by a corresponding increase in the basicity of the chrome liquors.

Another respect in which one-bath chrome tanning resembles the vegetable tannage is in the necessity for a gradual increase in the strength of the liquor, immersion in a strong liquor producing drawn grain and overtannage on the surface, which causes both brittleness and slow penetration. The comparative rate of increase may be much greater, however, in the case of the mineral tannage owing to its powers of quick penetration, the whole tannage often involving only a few hours, and never more than a few days. In the case of light goods (goat, sheep, etc.), the tannage is most conveniently brought about in paddles, though perhaps more economically in slowly revolving drums. Drums are usually used for heavier goods (calf, hides, etc.), but for the heaviest work (sole and strap butts, etc.) the tannage is often in pits or vats by suspension. Whichever class of goods are being tanned, and whichever method is employed, there are two methods of adding the chrome solution; either the same liquor may be used throughout the tannage, and its concentration increased gradually by the slow addition of a strong stock solution, or a series of different liquors may be given whose concentration is increasingly greater. Where the first method is adopted some care and economy is necessary in exhausting the liquor that is left when the tannage is complete. If the second method is employed with paddles a three-paddle system may be worked as in the sumach tannage of goat skins (p. 204); if used with drums, a three-drum

system may also be utilised, but the goods should remain in the same drum during the whole of the tannage and the liquors run off and pumped on to another pack of goods in another drum; if used in pits, the best plan is to work the liquors like a round of suspender-handlers as in vegetable tanning. In many cases it is convenient to combine these two methods, and it is clear also that systems of more than three paddles or drums may be employed.

The mode of penetration of the chrome salts through the pelt has given rise to much discussion, but the following view was held and taught by Procter for many years, and has recently been confirmed by the experimental work of Stiasny.

The chromic salts are well known to be hydrolysed in aqueous solution, and the work of Denham has shown that one can express the course of the hydrolysis by the following typical equations:—

(1) Blue chromic sulphate—moderately diluted.

$$Cr_2(SO_4)_3 + H_2O \rightleftharpoons 2\ Cr(OH)SO_4 + H_2SO_4.$$

(2) Blue chromic sulphate—largely diluted.

$$Cr_2(SO_4)_3 + 2\ H_2O \rightleftharpoons Cr_2(OH)_4SO_4 + 2\ H_2SO_4.$$

(3) Green chromic sulphate—moderately diluted.

$$\left[Cr_4(SO_4)_4\right](SO_4)_2 + 2\ H_2O \rightleftharpoons \left[Cr_4(SO_4)_4\right](OH)_2SO_4 + H_2SO_4.$$

(4) Green chromic sulphate—largely diluted.

$$\left[Cr_4(SO_4)_4\right](SO_4)_2 + 4\ H_2O \rightleftharpoons \left[Cr_4(SO_4)_4\right](OH)_4 + 2\ H_2SO_4.$$

The solutions contain, therefore, a basic chromium salt and free acid, and the view of Procter and Stiasny is that these act upon the hide fibres in different and totally unconnected ways. The free acid is in crystalloidal solution, penetrates quickly into the fibres, and is reversibly adsorbed by them. The basic salt changes by polymerisation into colloid complexes which, however, possess still considerable diffusive power, though much less of course than the free acid. This

basic part is also adsorbed gradually and undergoes the change of condition from "sol" to "gel" form, by which the irreversibility of the adsorption is caused. The separation from the solution of both products of hydrolysis effects a further hydrolysis in the sense of the above equations and further adsorption. Hence in the beginning of the tannage much free acid and little basic salt is taken up by the pelt, but in the further course of tannage the reception of the basic part becomes always relatively stronger, so that in practice the basicity of the tanning liquor at first quickly increases and then gradually decreases again. The reversibly adsorbed free acid can be removed by washing, but this is usually brought about in practice by "neutralising" (p. 355) with weak alkalies. Chrome liquors are also made "basic" before use by the addition of alkalies, which effects also a neutralisation of the free acid formed by hydrolysis.

Basic chrome liquors may be made in a variety of ways, the simplest perhaps of which is to add a solution of soda crystals to a solution of chrome alum. If the soda is added quickly chromium hydrate $Cr(OH)_3$ will, of course, be precipitated, but if the solution is poured in slowly and with constant stirring any precipitate of hydrate completely redissolves and a clear liquor is obtained. Sufficient alkali should be added to produce the salt $Cr(OH)SO_4$—*i.e.*, 1 molecule of chrome alum K_2SO_4, $Cr_2(SO_4)_3 24H_2O$ (mol: wt. 998) will require 1 molecule of soda crystals Na_2CO_3, H_2O (mol. wt. 286). Hence for every ten parts by weight of chrome alum used, 2·86 parts of soda crystals (1·06 parts of anhydrous carbonate) must be employed. It is convenient in practice to make a 10 per cent. stock solution of this liquor—*i.e.*, 10 lbs. of chrome alum are dissolved in 8 gallons of water, the soda solution added, and the total volume made up to 10 gallons. The soda may be dissolved in a small quantity of boiling water and the solution afterwards diluted to about a gallon with cold, but the chrome alum should be dissolved only in cold or tepid water, as in hot solution it splits up into a basic salt, and an acid salt, and complications in the tannage would arise therefrom. Each 100 lbs. of pelt requires fully 10 lbs. of chrome alum for a satisfactory tannage, and hence will

take 10 gallons of the stock solution. Eitner recommends neutralising the alum with hypo and boiling off the sulphur dioxide liberated. In the addition of soda there is no need to boil off the carbon dioxide, and this process is therefore easier and safer as well as cheaper.

Procter's glucose liquor is made up by dissolving 3 lbs. of potassium dichromate in a convenient amount of water, adding 2·5 lbs. of concentrated sulphuric acid (or 6 lbs. hydrochloric) and then glucose of good quality until the reduction is complete and a green solution obtained free from any yellowish tinge. About 3·5 lbs. of the sugar are usually required. A brisk effervescence occurs in the reduction due to the evolution of carbon dioxide, and it is necessary therefore to use a vessel of fair capacity. Other sugars—dextrin, glycerin, alcohol, organic acids and other substances may be used in place of glucose. The disadvantage of this liquor is that oxidation products of the glucose are of an uncertain nature, and are liable to affect the tanning properties of the solution to a varying extent. Practice has shown, however, that this bath will yield a plump and mellow leather from calf and hide. If the quantities mentioned above are taken, and the liquor made up to 10 gallons, the liquor will be of approximately the same strength as the basic chrome alum liquor before described—*i.e.*, the 10 gallons will be sufficient for 100 lbs. of pelt.

Many concentrated solutions of basic chrome salts are now on the market as "chrome extracts," that of the Martin Dennis Co.—"Tanolin"—being, of course, the oldest. It originally consisted merely of a basic chrome chloride, but now contains sulphates and other salts. Other preparations are also made by this firm. About 3 gallons of "Tanolin" are required for 100 lbs. pelt. Other preparations are "Vulcanochrom," "Corin," "Chromalin," "Progress tan liquor," and "Chromatine." They are of somewhat similar concentration, but contain usually more sulphates and chlorides, and often also aluminium salts. Eitner has also made some preparations, "Cromast," "Cromul," and "Cromar," containing organic matter, which is supposed to modify the annage and render it suitable for heavy leathers, upper

leathers, and light leathers respectively. In this country bought liquors are not very much used.

General qualities of chrome leather.—On this subject much might be said, but perhaps one of the greatest advantages of the chrome tannage lies in the quickness of the process when compared with the vegetable tannages. This enables the tanner to have a large turnover. Its waterproofness (after fat-liquoring, etc.) and compactness of substance have also assisted in making it extremely popular for upper leathers (box calf, glacé kid, etc.). Another great advantage of chrome leathers is in their great tensile strength as compared with the vegetable tanned leathers. This quality makes the tannage exceedingly suitable for picking bands, belt and strap leathers. On the other hand, the tannage is "empty," *i.e.*, it is apt to yield not merely light weight, but leathers devoid of solidity and firmness, and as a rule, therefore, there should be as little loss of hide substance as possible in soaks and limes, and the fermentation processes of deliming should, generally speaking, be substituted by the mere neutralisation of the lime with acids. Goat skins for chrome work, however, should be thoroughly puered to produce smooth grain. The isolation of the fibres is usually greater with chrome than with the vegetable tannages, and this causes a woolliness on the flesh side, which makes the goods unsuitable for finishing on this side. It also causes an unfortunate tendency to stretch, which is awkward in the case of belt and boot leathers. This defect can be minimised by using quick liming processes with sulphides, in which the hide fibres are not so much split up into their smaller constituent fibrils. The isolation of the fibres and contraction of the skins makes the substance more compact, however, and this is an advantage for sheep leathers. Different kinds of skin take up the chrome tannage in different degrees. Sheep skins, horse hides, and kips are apt to fix little chrome, but goat skins, ox hides, and especially calf skins, distinctly more. The basicity of the one-bath chrome liquors should therefore be modified accordingly. In the two-bath process the differences in absorption are less marked. The avoidance of drawn grain is also a difficulty, more especially with goat skins, and when formed

it can never be removed by mechanical treatment. Loose grain is a further difficulty which can only be satisfactorily overcome by a combination tannage of chrome and vegetable materials.

Equally good leather is produced by "two-bath" and "one-bath" processes, but the latter is the cheaper process, and is usually more convenient to manipulate. It has also the advantage that it does not give rise to the painful chrome sores which are very liable to occur with those who work in chromic acid liquors. The two-bath process is usually considered to give a more mellow tannage and a better colour than the one-bath, and this is generally accounted for by the

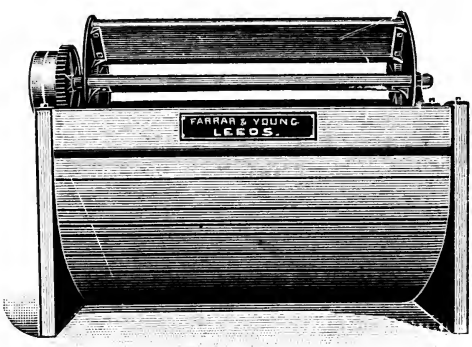


FIG. 59.—Tanning paddle.

presence of free sulphur in the leathers tanned by the former process. Broadly speaking, the two-bath process is more suitable for the lighter leathers. It is unsuitable for leathers that are to be japanned (p. 380). Combined one-bath and two-bath processes have been suggested in which chrome alum and potassium dichromate are employed together and thiosulphate used later. These processes, however, are not very widely used. It is more important for all chrome tannages to have the raw materials free from defects, warbles, scratches, etc., as these show more in the finished goods than with the vegetable tannages.

A brief description of some chrome tannages will now be given, all percentages having reference to 100 lbs. of wet untreated pelt, except where stated otherwise.

Calf skins and hides (for box calf, box sides, willow calf, enamelled calf, etc.) may be tanned by any of the following methods, but in this country the one-bath processes are more generally employed. Hides are cut into sides after unhairing, and are often split whilst full of lime ("green-splitting"), the grains being then tanned with chrome, whilst the fleshes are vegetable tanned and finished for waxed splits (see p. 303). It is, however, common to split after chrome tanning or colouring through, and the fleshes are then often re-tanned in the drum with extracts before currying.

(1) The following one-bath process is as cheap and satisfactory as any. The skins—after puering and drenching—are tanned by the basic chrome alum liquor. The liquor is made up with 10 per cent. of chrome alum on the pelt weight of each pack, to which has been added 3 per cent. of soda crystals (p. 223). The three-drum system mentioned above may be used for tanning. The green pack should receive first a liquor which has been used for two previous packs. It is then treated with a once-used liquor, and afterwards with a new liquor made up from chrome alum as described. A new liquor is therefore made for each pack of goods and exhausted by two following packs. A period of three to four hours in each liquor should be quite sufficient. By lengthening the time of drumming in the last and new liquor, and by adding some of the chrome solution after a time, it is quite practicable to work a two-drum system effectively. If, however, it is desired to work with one drum only, the goods should be started in sufficient water with a portion only of the chrome liquor, the rest of which should be gradually added at intervals of an hour or two. In this case also it is necessary to use 20 per cent. of chrome alum and 6 per cent. of soda to obtain the necessary strength of liquor for complete tannage. The liquor which is left over, strengthened with 10 per cent. chrome alum and 3 per cent. soda, may be used for the next pack in a similar manner.

This tannage is also satisfactory for goods which have been delimed by puering only, by drenching only, or by pickling. Sometimes goods are placed in a bath of alum and salt (5 per cent. of each) just before tannage, and, indeed, are occasionally

delimed by means of it, but it is doubtful whether there is any advantage gained by such treatment. The process is also satisfactory for goods which have just been delimed on the surface with lactic acid, but is apt to give a rather hard feel to the grain.

(2) Excellent chrome calf is also made by tanning with Procter's glucose liquor (p. 224), using 5 per cent. sulphuric acid, 6 per cent. potassium dichromate, and 7 per cent. of glucose on the pelt weight. This corresponds really to the use of about 20 per cent. of chrome alum. The liquor is more troublesome to prepare, and requires more care, and is therefore not so much used as formerly. The mechanical operations of this tannage may be just the same as described for the basic chrome alum liquor.

(3) In another one-bath method the skins are placed in a paddle with sufficient water to cover, and 5 per cent. alum and 10 per cent. salt are added. The goods are run for half an hour, and rather less than a gallon of the 10 per cent. basic chrome alum stock solution is added to the paddle liquor and the goods run another half-hour. Another gallon of stock solution is now added, and the goods run for one hour. Two gallons of stock solution are now added, and the paddling continued again for an hour. This last procedure is repeated until the tannage is complete, which will not be satisfactorily accomplished in less than 12 hours. The liquor left over may be used for the next pack of green goods if some alum and salt are added to it, but this must not be done more than twice.

(4) A two-bath process can be carried out in the following manner: The skins, after drenching, are placed in a solution of 10 per cent. salt in 15 gallons per cent. of water, paddled for 15 minutes, a diluted solution of 2 per cent. hydrochloric acid gradually added, and the paddling continued another quarter of an hour. The pickled skins are drummed half an hour in a solution of 2 per cent. potassium dichromate in 12 gallons per cent. water, and a solution of 4 per cent. potassium dichromate and $2\frac{1}{2}$ per cent. salt in 15 gallons per cent. water is added to the drum and the drumming continued till the goods are struck through, which will be in about four hours. They are then horsed up

overnight, struck out on the vertical table machine (p. 333), and passed through the hypo dip. This is made by dissolving 3½ per cent. thiosulphate in 18 gallons per cent. water. The main reduction bath is made up with 10 per cent. thiosulphate in 25 gallons per cent. water, and 5 per cent. hydrochloric acid is added. When the liquor turns milky the skins are quickly thrown in and the paddling continued for the rest of the day. The goods are left overnight in the liquor.

(5) Another method is to put the drenched skins without pickling into a paddle liquor of 5 per cent. potassium dichromate, 2½ per cent. hydrochloric acid, and 5 per cent. salt in 12 gallons per cent. water, and reduce as before. The chroming should require about six hours' paddling and the reduction about four hours' paddling. If chromic acid is employed 4 to 5 per cent. is taken and no hydrochloric acid is added, but the salt may be increased with advantage up to 10 per cent.

(6) Where the skins have been merely delimed with acid the first bath may advantageously consist of 5 per cent. dichromate, 5 per cent. hydrochloric acid, 1 to 3 per cent. aluminium sulphate, and 5 to 10 per cent. salt. The reduction bath should then contain 12 to 15 per cent. thiosulphate, and after the insertion of the goods and some paddling 4 to 5 per cent. of hydrochloric acid should be added slowly. Pickled goods may also be placed directly in the above chroming bath, if the quantity of salt be increased somewhat; and if the quantity of acid be increased, goods which have not been delimed may be placed in this bath.

(7) A further two-bath method is to give a pickle of 5 per cent. aluminium sulphate, 7½ per cent. salt, and 3 per cent. sulphuric acid in 6 gallons per cent. of water. The goods are then dried out for any sorting and trimming. They are wet back by handling for 15 minutes in a solution of 5 per cent. salt in 6 gallons per cent. water, and are then passed in the neutral chroming bath, in which 6 per cent. of dichromate is employed. The second bath should contain 15 per cent. thiosulphate and 4½ per cent. hydrochloric acid.

(8) Combined one-bath two-bath processes have also been used with this class of goods with some success. The author has made good chrome calf with a chroming bath of 20 per

cent. chrome alum, made basic with 6 per cent. soda, to which 2 per cent. of potassium dichromate had been added. The goods are started in a little water and the chroming liquor added gradually over a period of six hours, and after remaining in the bath altogether for 10 to 12 hours they are horsed up overnight in a brownish condition. They are then reduced with 5 per cent. thiosulphate and 2½ per cent. hydrochloric acid. Good results are also obtained if the glucose liquor be employed instead of the chrome alum liquor. Two per cent. of dichromate are added to a liquor made from 10 per cent. sulphuric acid, 12 per cent. dichromate and 14 per cent. glucose. The goods are chromed with this and reduced as before. The chroming liquor may be strengthened with half quantities, and used again for the next pack, but it is desirable to control the chroming process by frequent analysis of the liquor.

Goat skins (for glacé kid, dull kid, etc.) are perhaps most usually tanned by the two-bath process, but any of the following methods will give satisfactory results.

(1) After puering, they are washed for a short time in boric acid, drained, and weighed. They are then pickled in hydrochloric acid and salt and chromed in drum precisely as in process (4) for chrome calf, horsed up overnight to drain, and struck out by machine. The hypo dip through which they are next passed consists of 4 per cent. thiosulphate in 15 gallons per cent. water. After being again horsed to drain for a short time, they are put into a reduction bath of 10 per cent. thiosulphate in 20 gallons per cent. water. The skins are inserted quickly when the liquor turns milky, and, after paddling for some hours, are left overnight in the liquor.

(2) In another two-bath method the skins are both puered and drenched, but not pickled. A paddle is then filled with water, and a solution containing 1 per cent dichromate and ½ per cent. hydrochloric acid is added, and the goods inserted and paddled for some hours. The bath is then strengthened with 5 per cent. dichromate and 2½ per cent. hydrochloric acid slowly added over two hours, the paddling is continued another six hours, and the goods then horsed up overnight. After passing through a somewhat strong hypo dip, they are

reduced with 18 per cent. thiosulphate and 6 per cent. hydrochloric acid. The goods are inserted when the liquor turns milky, and more acid is added later if necessary.

(3) Where the skins are received in the pickled state they may be depickled in salt and whitening and possibly a little bicarbonate of soda, and afterwards washed, puered, and scudded. They may then be chromed with 6 per cent. dichromate and 3 per cent. hydrochloric acid, or with 5 to 6 per cent. chromic acid and 5 to 8 per cent. salt, and then reduced with 12 to 15 per cent. thiosulphate and 6 to 8 per cent. hydrochloric acid, the skins being inserted when the liquor turns milky.

(4) If the acid chroming bath is desired the skins should be first well depickled in salt and whitening. They are then placed in sufficient water in a paddle, and a solution of 4 per cent. potassium dichromate and 4 per cent. hydrochloric acid slowly added. In reducing the bath should consist of 12 per cent. thiosulphate, and the goods should be paddled in this for 20 to 30 minutes, then 5 per cent. hydrochloric acid should be added gradually in 8 to 10 small portions, more rapidly for small light skins and more slowly in the latter half of the operation.

(5) Another good two-bath tannage for goat skins is to chrome with 5 per cent. dichromate, 4 per cent. hydrochloric acid, and $2\frac{1}{4}$ per cent. aluminium sulphate. This is practically an acid bath, and hence reduction is with a bath of 20 per cent. thiosulphate, to which 5 per cent. hydrochloric acid is slowly added.

(6) In using the one-bath process it is often advisable to give a preparatory weak alum tannage. The skins are drummed in a liquor containing 3 per cent. aluminium sulphate, 4 per cent. sodium sulphate, and 5 per cent. salt[1], for three-quarters of an hour, and then horsed to drain for a few days, or possibly even dried out. Flour may be used in this bath, and in some cases also egg yolk and olive oil, and the goods dried out and "aged" as in tawing (p. 240). They are now wet back and drummed in water for three-quarters of an hour. The chroming liquor (10 gallons per cent. basic chrome alum liquor, or

[1] 8 to 9 per cent. of salt may be used, and the sodium sulphate omitted.

3 gallons per cent. "Tanolin," etc.) is now diluted somewhat and divided into three portions. One portion is added to the drum, the drumming continued for half an hour, a second portion added, and the drumming continued for another half-hour. The last portion is now added and the goods drummed until the tannage is complete, which will be in a few hours.

(7) In some cases it may have been desirable to pickle[1] with salt and acid, and if so the skins may be first wet down by drumming in a solution of 10 per cent. salt in 5 gallons per cent. water for five minutes. The depickling is then brought about by a solution made by dissolving 3 per cent. aluminium sulphate in 5 gallons per cent. water, and slowly adding to it, with constant stirring, a solution of 3 per cent. sodium carbonate in 5 gallons per cent. water. This solution is then added to the drum, and the goods drummed half an hour. The chrome liquor may then be added to the goods in the same drum and liquor as in the one-bath process just described. When the tannage is complete it is often customary to add ½ per cent. of sodium bicarbonate, drum another half-hour, and leave the goods in the liquor overnight.

(8) In many cases, however, it is sufficient to drum the skins for 20 minutes in a solution of 10 per cent. salt in 5 gallons per cent. water, and to add the chroming liquor gradually over a space of three hours. When the tannage is complete, the drumming is stopped, and the goods left overnight in the liquor.

Sheep skins (for imitation glacé, etc.) are treated somewhat similarly to goat skins, but it is essential to degrease these skins by pressure or by extraction.

(1) If tanning by the two-bath process the skins may be placed in the drum with sufficient water, and a solution of 5 per cent. dichromate and 2½ per cent. hydrochloric acid and up to 5 per cent. salt is gradually added to the drum. Motion is given till the chrome has evenly struck through, which occurs in a comparatively short time with these goods. Chromic acid may also be used, 4 to 5 per cent. being taken

[1] Pickles for chrome may be made fairly strong; in some American factories 5 per cent. of vitriol and 20 to 25 per cent. salt are employed, whereas for dongola 1 per cent. acid and 10 per cent. salt is sufficient.

with no acid but somewhat more salt. After horsing to drain and striking out they are reduced with 12 to 15 per cent. thiosulphate, and 3 per cent. hydrochloric acid is gradually added to the paddle liquor. If the skins are pickled, they may be depickled with salt and whitening or with the basic aluminium sulphate solution as described for pickled goatskins.

(2) If it is desired to use an acid chroming bath the following will be found to give good results: 5 per cent. dichromate, 5 per cent. hydrochloric acid, and 10 per cent. salt in 40 gallons per cent. water. When the skins are thoroughly struck through they are horsed up overnight and reduced in 20 per cent. thiosulphate to which 5 to 7 per cent. hydrochloric acid may be slowly added after about half an hour's paddling.

(3) If tanning by the one-bath process the skins are nearly always tawed first in alum and salt. They are depickled therefore with salt and whitening or C.T. bate and soda.[1] Then they are drummed in a solution of 3 per cent. aluminium sulphate, 6 to 8 per cent. salt (and possibly 4 per cent. sodium sulphate) for three-quarters of an hour, and horsed up to drain as long as possible. They are then tanned by the gradual addition of the basic chrome liquor as described for goatskins. It is also possible to taw as described and proceed immediately with the chrome tannage by adding the chrome to the drum in the usual way. If the skins have been wet down in a solution of 10 per cent. salt in 5 gallons per cent. water, and depickled with the basic alum solution, the chrome tannage may be commenced after 30 minutes' drumming. This one-bath process is considered to give the best results for this class of goods.

Sheep skin splits for "chrome-chamois" may be given the following tannage. After puering heavily, they are placed in a pickle of 6 per cent. sulphuric acid and 24 per cent. salt. They are paddled in this for three-quarters of an hour and 4 per cent. of potassium dichromate is added in two portions, the goods being run till well struck through. After horsing up overnight they are reduced with 15 per cent. thiosulphate, to which is

[1] 1 lb. of soda to every 2 lbs. bate.

added, after one hour's paddling, 1 per cent. of hydrochloric acid. The neutralisation (p. 355) is with 1 per cent. soda.

Picking band butts are now extensively chrome tanned, and have largely substituted the vegetable product on account of their greater durability, tensile strength and cleanliness.

(1) After a very short sulphide liming they are bated (or delimed with acids), drenched, and pickled in 10 per cent. salt and 10 per cent. sulphuric acid. The pickle should be about 6° Bé., and the goods are drummed in it for three to four hours, left overnight, drummed again for two hours, and horsed up. The goods then receive the acid chroming bath at 1° Bé., in which 2 per cent. dichromate and 4 per cent. hydrochloric acid are employed together with some salt. They are drummed in this two hours, and the penetration of the chrome completed by giving two hours on the horse. The hypo bath consists of a vat at 10° Bé., which may be used repeatedly for a week or two if strengthened up with 8 per cent. thiosulphate for each pack. The goods remain in this bath about six hours, and no further neutralisation (p. 355) is needed.

(2) Another two-bath process is to delime with lactic acid and chrome immediately in 2 to 5 per cent. dichromate, 2 to 5 per cent. hydrochloric acid, 4 per cent. aluminium sulphate, and 15 per cent. salt, and reduce in 5 per cent. thiosulphate to which 2 per cent. hydrochloric acid is slowly added.

(3) A heavier tannage may be given by chroming the delimed goods in 6 per cent. dichromate, 6 per cent. hydrochloric acid, and 10 to 15 per cent. salt. The goods are inserted in the hypo bath (15 per cent. thiosulphate) for three hours, and 3 to 5 per cent. hydrochloric acid is gradually added.

(4) A one-bath process may be carried out in the following manner: The butts are bated fairly low, scudded well, and bate shaved. The tannage is accomplished by suspension in a round of four large vats, giving three days in each vat. The liquors should be kept up to their strength by the addition of basic chrome liquor at the end of the first and second days. The barkometer may be used to judge this. At the end of the third day a shift is given; the tail liquor is run down the drain and a new liquor made up in the same vat, and the

goods shifted round, the old second liquor being used as the first without any strengthening. The tannage therefore lasts 12 days, but an extra vat may be given if necessary. If the basic chrome alum liquor is employed, the strongest vat should never take above 16 gallons of this per 100 gallons of water. A little aluminium sulphate may be beneficial, but salt should be avoided. If "Tanolin" is employed, the head liquor should be a 5 per cent. solution, and the other liquors of 4, 3, and 1½ per cent. strength respectively.

(5) The combined one-bath and two-bath process can be used for picking band butts. According to Eitner, the liquor is made with 3½ kilos. (7½ lbs.) chrome alum and 150 grams (5 ozs.) dichromate per butt. The goods are drummed in a good quantity of water, half this liquor added, and the drumming continued for three hours, and then stopped for an hour. The second half of the liquor is now added, and the goods run three hours and stopped one hour as before. Further drumming is given if necessary. The butts are olive green, and the reduction is completed with 800 grams (1¾ lbs.) of thiosulphate, and 500 grams (just over 1 lb.) of whitening per butt.

Motor butts, strap butts, and harness backs, are delimed with acids, or very lightly bated, and are tanned out in suspension as in the one-bath process for picker band butts. They may also be tanned in drums, but the two-bath process is not found to give the best results with these leathers. It has been found an excellent plan with these goods to give them a bath of normal chrome alum of 1° Bkr., in which they are handled twice a day for a week, and then to proceed with the one-bath tannage.

Sole butts[1] should be only surface delimed, in drum or pit, and then inserted into a solution of 6 per cent. aluminium sulphate, and when this has penetrated they are placed in a solution of 8 per cent. thiosulphate for 24 hours, which not only fixes the previous alum tannages, but causes a deposition of sulphur which is beneficial both to the quality and colour of the goods. The butts are then tanned out with

[1] The one-bath process is usually employed for these goods, but where colour is of importance, *e.g.*, for tennis boot soles, &c., the two-bath process is an advantage.

the one-bath process. If this is done in drums, the basic liquor (10 gallons per cent.) is added in three portions, one in the early morning, a second in the late afternoon, and the third next day, the tannage being complete before that day is over. It is, however, better to give a longer time. Another method is to have a series of five pits of 10°, 20°, 30°, 40°, and 50° Bkr. respectively. The goods should be 2 days in the first two pits and 1 day in each of the rest.

The Analytical Control of the chrome tannages is much simpler than the vegetable tannages on account of the definiteness of the materials.

In the **two-bath process** the composition of the liquors may be readily determined as follows :—

(1) 10 cc. of the liquor are placed in a ¼ litre stoppered bottle, 5 cc. concentrated hydrochloric acid, and 10 cc. of 10 per cent. potassium iodide solution are added. After shaking and allowing to stand a few minutes, the liquor is then titrated with N/10 sodium thiosulphate in the presence of 1 cc. freshly made starch infusion until the intense blue colour due to the liberated iodine has given place to the pale green of the chromic chloride. Each cc. of thiosulphate solution corresponds to 0·0033 grams CrO_3, 0·0049 grams $K_2Cr_2O_7$, or 0·00647 grams K_2CrO_4.

(2) 10 cc. of the liquor are titrated with N/10 caustic soda in the presence of phenol-phthalein. Potassium chromate is neutral to phenol-phthalein, and chromic acts therefore as a dibasic acid. If the acid chroming bath is being used the excess of hydrochloric acid will also be determined here. More indicator should be added in the course of the titration on account of its oxidation by the chromic acid. Each cc. of soda solution corresponds to 0·005 grams free CrO_3, 0·01 grams "half bound" CrO_3 (*i.e.* present as $K_2Cr_2O_7$), 0·0147 grams $K_2Cr_2O_7$, or 0·00365 grams HCl.

If determination (1) takes *a* cc. N/10 thiosulphate, and determination (2) *b* cc. N/10 caustic soda, the nature of the liquor can be gathered from the table on opposite page.

If aluminium salts are present these calculations will not apply accurately, and if chromic salts are present the analysis becomes exceedingly complicated.

(3) 10 cc. of the liquor are made neutral by the addition of magnesia and titrated with N/10 silver nitrate until the brick-red of silver chromate permanently appears. Each cc. of silver nitrate solution corresponds to 0·00745 grams KCl, 0·00585 grams NaCl or 0·00365 grams of hydrochloric acid.

If—	Liquor consists of—	Hence 10 cc. liquor contain—
b is less than $\frac{1}{3}\,a$	potassium chromate and potassium dichromate	$(b \times 0{\cdot}0147)$ gms. $K_2Cr_2O_7$, and $\{(a \times 0{\cdot}0033) - (b \times 0{\cdot}01)\}$ 1·94 gms. K_2CrO_4.
b is equal to $\frac{1}{3}\,a$	potassium dichromate only	$(a \times 0{\cdot}0049)$ gms., or $(b \times 0{\cdot}0147)$ gms. $K_2Cr_2O_7$.
b is greater than $\frac{1}{3}\,a$, but is less than $\frac{2}{3}\,a$	potassium dichromate and chromic acid	$\left[(b - \frac{1}{3}\,a) \times 0{\cdot}01\right]$ gms. CrO_3, and $\left\{(a \times 0{\cdot}0033) - \left[(b - \frac{1}{3}\,a)\,0{\cdot}01\right]\right\}$ 1·47 gms. $K_2Cr_2O_7$.
b is equal to $\frac{2}{3}\,a$	chromic acid only .	$(a \times 0{\cdot}0033)$ gms., or $(b \times 0{\cdot}005)$ gms. CrO_3.
b is greater than $\frac{2}{3}\,a$	chromic acid and free hydrochloric acid	$(a \times 0{\cdot}0033)$ gms. CrO_3 $\{(b - \frac{2}{3}\,a) \times 0{\cdot}00365\}$ gms. HCl.

(4) The thiosulphate in a hypo bath may be estimated by adding the liquor from a burette to a $\frac{1}{4}$ litre stoppered bottle containing 10 cc. of 10 per cent. potassium iodide, 5 cc. concentrated hydrochloric acid, 20 cc. N/10 potassium dichromate and a little fresh starch solution. The volume of the hypo liquor required for the titration contains 0·496 grams pure sodium thiosulphate.

In the **one-bath process**, what is usually required is the concentration and basicity of the solution,[1] *i.e.* the strength in chromium and the amount of acid radicle combined with it.

(1) *Chromium.*—A quantity of liquor to contain 0·3 to 0·5 grams Cr is measured into a rather large beaker and diluted (if necessary) to about 100 cc. with distilled water. To this cold solution 3 grams of sodium peroxide are added in successive

[1] Procter and McCandlish, J. S. C. I. 1907, 458.

quantities of 1 gram. A clock-glass should be over the beaker and rapidly replaced after each addition. When effervescence has ceased, the liquor is stirred up with a glass rod, gradually heated up and boiled quarter-hour to destroy all excess of peroxide. The liquor is cooled, made up to 250 cc., and 50 cc. of this are acidified with hydrochloric acid, 10 cc. of 10 per cent. potassium iodide are added, and the liberated iodine titrated with thiosulphate as in the two-bath chrome liquor. Each cc. N/10 thiosulphate corresponds to 0·00173 grams chromium.

(2) "*Basicity.*"—A quantity of liquor to contain about 2·5 grams of chrome alum or its equivalent is diluted with distilled water in a suitable porcelain basin to about 200 cc., and 3 to 4 cc. of 1 per cent. phenol phthalein solution added. The liquor is now boiled and titrated whilst boiling with N/1 caustic soda, stirring constantly until a permanent pink is obtained in the clear liquor. Each cc. N/1 caustic soda corresponds to 0·0355 grams Cl or 0·048 gram SO_4 combined with chromium. If aluminium or iron salts are present the ratio Cr : SO_4 determined above will be affected, and the amount of iron and aluminium must be determined and allowance made.

CHAPTER XVIII

ALUM AND COMBINATION TANNAGES

The theory and nature of the mineral tannages has been explained to some extent in the previous chapter, in which it was pointed out that no aluminium salts gave a satisfactory leather when used alone, and that in making them basic the range of basicity allowable was much narrower than in the case of chromium salts. Hence all the alum tannages employ also other materials which minimise or hide the defective properties of the normal alumina salts by the introduction of their own characteristic effects. In the manufacture of glove kid, which may perhaps be taken as the typical illustration of the alum tanned or "tawed" leathers, there is employed usually, in addition to alum, varying amounts of salt, flour, egg-yolk and olive oil. That the effect of the salt was to assist in the production of a soft leather has long been known, but the explanation is due to Procter. "Alumina is a weak base which readily gives up its acid to the pelt, being converted into a basic salt. The acid not only swells the pelt and renders it incapable of producing a soft leather, but the swollen pelt is less ready to absorb the alumina salt, and so remains undertanned. The addition of salt prevents the swelling effect of the acid, and produces a partial pickling of the skin, which in conjunction with the basic alumina salt formed, yields a satisfactory leather, though one which is readily affected by washing."[1] If too much salt be used, however, it is apt to injure the gloss of the grain in finishing and make the leather somewhat moist. The egg-yolk acts mainly by the oil it contains.[2] It gives softness, fulness, stretch, and permits a glossy finish. Any olive oil which may be used acts similarly and is a partial substitute for egg-yolk, but if

[1] Procter, "Principles of Leather Manufacture," p. 186.
[2] About 30 per cent.

used too freely gives a damp and smeary feel to the leather. It will be seen, however, that tawing is to some extent a fat tannage. Flour acts as a whitening and filling agent and assists also in the emulsification of the olive oil, so that with more flour, more oil can be used. These materials are made into a paste with water and the goods drummed with the paste and dried out. The goods are kept in the dry condition for several weeks to "age," in which time the alum salt becomes more firmly fixed in the fibre and the tannage therefore more thorough. In the finishing processes, however, considerable amounts of all these materials are washed out and have to be replaced by further treatment (re-egging, p. 371). Furthermore, in finishing it is impossible to obtain a satisfactory glaze on the grain without some degree of vegetable tannage, and hence in the manufacture of French glazed kid it is necessary to brush the grain at least with infusions of the vegetable tannins, this operation being often actually combined with the dyeing process. Danish and Swedish glove leathers were similarly coloured after tawing and to some extent tanned with vegetable materials. Combination tannages therefore have been devised in which the characteristics of both mineral and vegetable tannages have been blended. It has been pointed out that the mineral tannages give soft and tough leathers, in which the fibres are well isolated, and hence allow "stretch," but that they lack solidity and plumpness and give a woolly flesh. Such leathers when re-tanned with vegetable materials retain these properties in a large degree, and hence are only suitable for grain finishes or "velvet" fleshes. On the other hand, leathers which have been vegetable tanned and afterwards tawed retain also the plumpness, fulness and resistance to water which is typical of the first tannage, and yet receive also the characteristic softness of the alumed leathers. Thus it is evident that the properties of a combination tanned leather are generally nearer to that tannage which has been first applied. The introduction by Kent of "fat-liquoring" (p. 356), by which an emulsion of soap and oil could be substituted for the expensive egg-yolk, and softness thereby obtained without greasiness, made possible the commercial success of combination tannages. Dongola leather, made by

giving the skins a preliminary vegetable tannage and afterwards treating with alum and salt and lightly fat-liquoring, became therefore a serious competitor to glazed kid, and this type of tannage was soon applied also to the production of other leathers for shoe purposes. Dull finishes are, however, best obtained by tawing first and then tanning with vegetable tanning materials. The combination principle is also used in the manufacture of the so-called "green leather" (for belt laces, picking bands, combing leathers, etc.), in which both toughness and flexibility are required. The introduction of the chrome tannage made possible also another type of combination leathers, and in this case also the same general principles apply. Leathers well tanned with vegetable materials are little affected by subsequent treatment with basic chrome salts, but it is a curious fact that the fully chrome tanned leathers can absorb considerable amounts of the vegetable tannins, though the leathers produced are not of good quality. If, however, the vegetable tannage has not gone far it is possible to chrome afterwards and obtain leather which has many of the characteristic qualities of the pure chrome tannage. Thus East India tanned sheep and goat skins and kips, when washed to remove superfluous tan, may be chromed by the one-bath process and finished as for glacé kid and box calf. The two-bath process is, however, not suitable for chroming leathers which are lightly vegetable tanned, on account of the oxidising action of the chromic acid on the tannins. The use of a light alum tannage as a preparation for the chrome tannage is another type of combination which has already been discussed.

Lamb skins or kid skins for glove kid after puering and drenching, are tawed in the following manner. The flour is made into a paste with tepid water, and egg-yolk somewhat diluted with warmed water, strained if necessary, and mixed in along with any olive oil. The alum and salt are dissolved in water and the solution heated to 50° C. and added to the mixture, which should then be about 40° C. This constitutes the tawing paste. As to the exact quantities to be taken there are wide differences in the many recipes that have been given, but the following may

be taken as somewhat typical.[1] For every 100 lamb skins take :—

	Light skins.	Medium skins.	Heavy skins.[2]
Flour . .	2½ to 3 kilos.[3]	3½ to 4½ kilos.	5 to 6 kilos.
Alum . .	1 to 1¼ kilos.	1½ to 1¾ kilos.	2 to 3 kilos.

Salt should be used one-third the weight of the alum employed, and 12 to 14 egg-yolks should be taken for each kilo. of flour, and the water required is 2 to 3 litres for each kilo. of flour. One litre of preserved egg-yolk may be substituted for 50 egg-yolks.

In this paste the skins should be drummed for an hour or more according to the thickness and nature of the skins. They are then dried on poles, grain outwards. The drying should be rapid, but not warm, and therefore good ventilation is essential. They are then damped back by passing rapidly through tepid water and staked (p. 359) damp, nearly dried, and again staked. They are then " aged " for several weeks.

Calf skins for calf kid, after drenching, are tawed in a similar way to lamb skins for glove kid. Procter gives the following paste : 5 per cent. flour, 2½ per cent. alum, 1 per cent. salt, 1½ per cent. egg-yolk, 2 ozs. per cent. olive oil, and 1¼ to 1½ gallons per cent. of water. Several hours drumming are required for thick skins, but the drum should be stopped at frequent intervals in order to prevent heat due to friction. The goods are next allowed to lay in pile overnight to complete the absorption of the tawing paste, and are sometimes placed in special tanks, where they may remain several days. They are now split in the band-knife machine (p. 281) and dried out rapidly in a good draught, cool at first, but afterwards raising the temperature to 40° C., and falling again to 32° C. as the skins approach dryness. Too great heat makes the skins hard or tender, too damp heat makes them spongy, and too slow drying makes them harsh and lacking in stretch.

[1] Eitner, Gerber, 1900, p. 271.
[2] A *heavy* skin corresponds to about 1 kilo. of pelt.
[3] A " kilo." is 2·2 lbs. approximately.

They are now aged for several weeks in a cool, dry place. Continental skins for calf kid are often split before tawing, which not only saves expense but permits a greater scope in the disposal of the fleshes.

Goat skins for glazed dongola form a good illustration of the combination tannages. The skins are puered and drenched in the usual way and placed in large paddles, where they first receive a slight gambier tannage, using 4 lbs. block gambier for each dozen skins. Somewhat later ½ lb. alum and ¼ lb. salt per dozen skins are added to the same liquor and the paddling continued until the tannage is complete, which is usually in about twenty-four hours. The skins are then washed well in tepid water to remove superfluous tan—mineral and vegetable—and are then ready to be fat-liquored, without any ageing

Modifications of the dongola tannage are practically infinite, for it has been adapted for use with sheep skins, dog skins, calf skins and hides in the production of all manner of glove and upper leathers, so that it is useless here to attempt more than a brief indication of some of the various lines of operation.

The lightly tanned E. I. skins (sheep or goat) may be finished for dongola by washing in weak borax and passing through a weak "sour" (see p. 332), and then drumming with 10 per cent. alum and 5 per cent. salt, and washing and finishing as usual. They may also receive a basic alum re-tannage, using soda one-third the weight of the alum, and employing flour if necessary to fill and plump.

Dog skin glove leathers, from dog skins or sheep skins, also receive the vegetable tannage first. A clear gambier liquor is usually employed for this tannage, to which an infusion of young fustic and other dyewoods has been added. The goods are drummed in 15 gallons per cent. water and the gambier and dyewood liquor is added to the drum in twelve portions at half-hour intervals. The goods are then struck out and tawed with 14 per cent. flour, 2 per cent. salt, 5 per cent. alum, and 0·4 gallons per cent. egg-yolk.

Hides may be finished for dongola after the following tannage. They are unhaired from sulphide limes, bated and

pickled. They then pass into a liquor of gambier about 6° Bkr. to which 10 lbs. alum and 7 lbs. salt are added for each 100 gallons. The goods are handled in this liquor for three days, strengthening each day, and are then drained to split and shave. They are then re-tanned for three days in gambier only at 18°—20° Bkr., strengthening daily.

Coloured dongola calf approximates even more closely to the vegetable tannages. The skins are tanned for 7 to 14 days in weak bark liquors and are then given the dongola tannage in alum, salt, and gambier for another week. This latter operation is best done in paddles which are run only intermittently.

For dull dongola the goods are first tawed in aluminium sulphate and salt, and often dried out and staked. They are afterwards re-tanned in drum with gambier. Suède and velvet-calf also receive the tawing first, flour and oil being used, but no egg-yolk. They are re-tanned in gambier.

Alum and salt are also used for the preparation of many kinds of white leather, laces for belts, "skivers" for chemists' bottles, whip lashes, sheep skin aprons, and in the dressing of wool rugs (Chap. XXIX) and other skins which are not unhaired. Flour is also employed, but no egg-yolk. Whitening is sometimes used to neutralise some free acid and to improve colour.

CHAPTER XIX

FAT, OIL, AND ALDEHYDE TANNAGES

The production of leather by means of oils and fats is almost as ancient as leather itself, this being without doubt one of the methods of primitive man, but the use of aldehydes for leather manufacture is of comparatively recent introduction, and at first sight there would seem no obvious connection. It is now known, however, that many of the typical oil or fat tannages include also an aldehyde tannage, and it is therefore convenient to treat all together.

The fat tannage pure and simple consists merely in subjecting the goods to more or less continuous motion, applying at intervals oils or soft fats and slowly drying out the moisture from the fibres. As the fibres contract in drying the fats are worked in between them by the mechanical treatment which the goods undergo. This fulfils the essential requirements for leather formation previously discussed,[1] viz., the drying of the fibres in a separate and non-adherent condition, which is ensured by the motion given, and also the coating of the fibres with a waterproof material. The precise mode of treatment varies considerably, of course, but this is practically the principle on which the so-called "Crown," "Helvetia," "Rawhide," and other fat-tanned leathers are manufactured. The alternative to a waterproof coating of the fibre is that there shall be some chemical action on the fibres which shall render them impervious to water, and this is realised in the pure aldehyde tannages, such as the formaldehyde process. In the so-called oil tannages, however, we have a distinct combination of these methods, for the goods are not only stocked with oil and dried, but a vigorous oxidation is also permitted in which aldehydes (acrolein, etc.) and other insoluble oxidation products are formed, the former tanning,

[1] See p. 211.

by virtue of its chemical activity, and the latter also mechanically, coating the fibres. This is the principle underlying the manufacture of chamois, buff, and buck leathers. In the fat tannages there is nearly always some degree of "chamoising," for there is always a little oxidation of the fats used, but in these cases the non-drying and less oxidisable fats are used, so that this is only true in a comparatively small degree. It should be perhaps noted here that many leathers are treated with oils and fats after being tanned with other materials, vegetable and mineral, and that this in many cases practically amounts to a subsequent fat tannage.

Helvetia and Crown leathers are made in the following way. The hides receive a somewhat long liming, and after unhairing and fleshing, are delimed by drenching, scudded well and fleshed again, and sometimes coloured with a weak tan liquor. They are then partially dried with a fan draught, rolled into bundles and drummed in a warm drum for some hours. They are then taken out, and after a little further drying are coated with the tanning paste. This was composed originally of flour, ox-brains, butter, milk, and soft fats made into a paste with water, but it is now known that the essential ingredients are merely the soft fats, the emulsification of which is assisted by the starch of the flour. The albuminous gluten of the latter is also absorbed. A good mixture can be obtained from seven parts of flour, seven parts of horse tallow or other soft fat, two parts of mutton tallow and one part of salt, made into a paste with four parts of water. A little degras or cod oil is also sometimes used. The mixture is pasted on the goods, which are drummed again at 35° C. for several hours (three to eight according to the thickness of the goods) and then taken out and dried further. The hides now receive a further coat of paste and more drumming, and these operations are repeated again if necessary in order to get in as much as possible. They are now ready for finishing.

Other fat tannages are on very similar lines. The South African "Reims," for example, are made by a continuous twisting of the thongs whilst drying, and intermittent application of the fats. The American rawhide leather is manufactured by drumming the imperfectly delimed goods

with tallow and neats-foot oil at a somewhat raised temperature for 24 hours.

Chamois leather is manufactured from the flesh splits of sheep skins. These are given a thorough liming (10 to 14 days), after splitting, using sharp limes and hauling each day. They are now levelled by the "frizer," who scrapes the skins over the beam with a sharp knife like that used in fleshing, and thereby removes all rough surface and loose fatty portions. The skins are then washed in running water and drenched 12 to 24 hours with constant handling, or drenched in paddle five to six hours. All superfluous liquor is now removed by pressing for an hour or so in the hydraulic press, after which the skins are separated and allowed to cool on a clean floor. The skins are then stocked or "milled" half an hour in the ordinary faller stocks, which equalises the moisture still remaining in them. They are now removed from the stocks and are thrown back one by one, sprinkling each skin with cod oil on both sides. The stocking is continued for three to four hours and the goods are then taken to the sheds and hung up by a hind shank for a day or more, and dried without heat until they become opaque. They are now re-sprinkled and re-stocked for three to four hours, and are dried further at 38° C. until of a brownish colour. The stocking distributes the oil evenly over and through the goods, and causes the heating of the goods and oxidation of the oil. The stocking and drying are repeated several times, using hotter stoves for each drying, and hanging closer together. Finally a "heater" is given in which the skins are hung quite close to each other by the neck, the temperature being 62—70° C. During the drying processes, pungent vapours are evolved of acrolein and other products of the oxidation of the oil. It is necessary that the first dryings should not be too quick, or parts of the skin may be unsaturated with oil and dry out transparent and horny.

After coming from the "heater" the skins are quickly packed into special bins or boxes, covered with matting, and allowed to heat spontaneously, which process is exceedingly delicate and needs careful attention. Occasionally they are "turned" into another empty box, with possibly some little

cooling before repacking, and this treatment is now continued until the oxidation is complete and the goods are thoroughly "heated off." Too much oil or too much moisture will cause defective places ("burns"), and when these appear on any skin it should be removed from the pack. The goods are now a dark-brown colour, and they are spread on a clean floor to cool.

The "wash-house" treatment involves the removal of the excess of oxidised oil products. The leather is dipped into water at 43° C. for a short time, and then pressed in the hydraulic press. The greasy water which first exudes is collected separately and the water allowed to settle out. The thick yellow oil (*degras*) which follows is collected in barrels and sold for leather dressing (see p. 302). A further quantity of somewhat inferior quality is obtained by paddling the skins in a hot alkaline solution. About 12 lbs. of soda crystals or its equivalent in soda ash should be used for each 20 to 25 dozen skins, and the goods paddled two hours in the liquor at 50° C. The liquor is then run off and the *sod oil* in it is recovered by the neutralisation of the alkali with sulphuric acid. The skins are now paddled with hot water (up to 60° C.) for an hour, fat-liquored (or "nourished") in paddle with cod oil and soft soap for one hour, put through the wringing machine or hydro extractor, and dried out. This is "crust" chamois leather.

In France the skins are generally oiled out on tables, folded into bundles, and then stocked. Seal oil and whale oil are also to a large extent used instead of cod oil. The heating is by suspending on hooks in warm stoves; but the oxidation is much more moderate and the oil therefore much less thickened. After dipping through hot water the skins are put into the hydraulic press or wringing machine, and the expressed oil constitutes pure *moellon*, which, when mixed with other fish oils, tallows, etc., yields commercial degras. More degras of inferior quality is subsequently recovered by the use of soda. In the old English process the oxidation was such that no oils could be recovered by pressure alone, and the skins were therefore treated at once with hot soda solution.

Buff leather is a somewhat similar product obtained from hides. Flat hides are desirable, but a good grain is not essential. They are limed 10 to 14 days in mellow liquors,

unhaired, fleshed, and limed again for a week or more in sharp limes to open up the spaces between the fibres. The grain is now "frized" off by a sharp knife over the beam, or a thin grain split is removed by the band-knife machine. This assists in the penetration of the oil. After frizing, they are rinsed through water, scudded flesh and grain, and sometimes surface delimed and again worked over the beam They are now hung up to dry with most of the lime still in them.

When stiff, they are stocked for two hours to soften and distribute the moisture evenly, and laid out to cool. They are then thrown into the stocks again, sprinkling with cod oil as for chamois. About 1 quart of fine slaked lime should have been thoroughly mixed with every 3 gallons of oil. After three to four hours' stocking, they begin to heat and are covered with lime soap. They are then hung up to dry in a moderately warm stove, and when thoroughly dry are re-sprinkled, re-stocked and re-dried. This treatment is continued for four to six days, gradually increasing the temperature of the stove up to 30° C. The goods are now hard and dry and possess a dirty-brown colour. The wash-house treatment is also similar in principle to that for chamois leather. The hides are placed overnight in a soda solution at 45° C. and scudded over the beam. They are now drummed for two hours in the same liquor, heated up to 50° C. This liquor is now run off and the sod oil recovered with sulphuric acid. The hides are drummed a further one and a half hours in another soda liquor at 55° C., and after some washing are fat-liquored as for chamois and dried out in a warm stove.

Occasionally degras is also obtained from these goods. On coming from the hot stove they are thrown into water at 30° C., and after some soaking are put through a wringing machine or between two spiral blades, and the degras thus removed. They are then put into a soda solution 2° Bé. at 27° C., rinsed through water, and put through the wringing machine again, and the sod oil separated from the lye by means of sulphuric acid. The hides are fat liquored and dried out.

Buck leather is made from deer skins. These are limed like hides for buff leather, but after washing are delimed by drenching and pressed to remove superfluous water. They

care, however, neither frized nor split at this stage. The skin are now stocked with oil just as for chamois leather, but for a longer time, as the penetration of the oil has not in this case been assisted by the removal of the grain. After "heating off" as for chamois, they are taken to the wash-house, immersed in hot water and pressed. They are now immersed in a solution of caustic soda at 45° C. until the grain is almost rotted, removed on to the beam and the grain pushed off with a sharp knife. The goods are now drummed in a sodium carbonate solution at 50° C., washed, fat-liquored, and dried out. A considerable quantity of "mock buck" is now manufactured from sheep skins and other cheaper raw material.

Formaldehyde leather is made under the patent of Payne and Pullman[1]. According to the specifications, about 4 cwt. of pelt is drummed with 100 to 120 gallons of water at 100° F., and the "dressing liquor" is added in successive quantities of 1 gallon at intervals of 15 minutes or more. This liquor consists of 16 lbs. of a solution of formaldehyde (containing 36 per cent. H.CHO) and 32 lbs. of sodium carbonate (80 per cent, Na_2CO_3) dissolved in 10 to 15 gallons of water The tannage is complete in three to six hours for light goods and in 12 to 48 hours for heavy goods, and towards the end of the operation the temperature is raised to 118° F. The excess of alkali is removed by drumming or paddling with a weak solution of ammonium sulphate (16 lbs. of 95 per cent. salt in 100 to 120 gallons) at 100—120° F. The goods are then "nourished" in a solution of 10 lbs. soft soap and 10 lbs. common salt in 80 gallons of water for about three hours with light goods, and about six hours for heavy goods. They are then dried out and finished.

The leather obtained bears considerable resemblance to buff leather, as would be, perhaps, expected from the nature of the process, but it is quite white, and hence needs no bleaching (ctr. p. 377). The function of the alkali in the process is somewhat obscure, and it is said that neutral or acid solutions of formaldehyde will also yield a satisfactory commercial product. The use of other alkalies and aldehydes is covered by the patent.

[1] Eng. Pat. 2872, 1898.

CHAPTER XX

THE DRYING OF LEATHER

The important operation of drying leather consists in the removal of all excess of moisture—*i.e.*, leather is considered dry when it does not lose weight if exposed to air at an ordinary temperature and degree of dryness by the evaporation of the moisture it may still contain. Leather is dried by allowing the superfluous moisture to evaporate into the air, and the principles of leather drying are therefore governed by the laws relating to the evaporation of liquids. Now air has at any temperature a definite limit in its capacity for water vapour, which limit is called the point of saturation, and it is clear, therefore, that air saturated with water vapour will have no drying power whatever, and that the drying power of air unsaturated with water vapour is dependent upon the amount of moisture it is still capable of receiving before becoming saturated. The rapidity of the evaporation of excess moisture and the rate of drying is, therefore, determined by the degree of saturation. Air always contains a considerable amount of moisture, and in this country the average humidity is about 82 per cent. of saturation, varying roughly between 70 and 90 per cent. according to the season. It will thus be readily understood that the amount of water to be evaporated from a pack of wet goods is far greater than the capacity of the ordinary air which immediately surrounds it, and hence that this air must be constantly removed and replaced by air of less saturation, or its capacity for water vapour must be increased by raising its temperature. In practice it is generally found advantageous to combine these two methods, and hence there arises the necessity for a definite and thorough system of ventilation and for a method of raising and controlling the temperature of the air which is supplied.

The maximum capacity of air for water vapour increases

very rapidly as the temperature rises, as is illustrated in the following table, which gives the weight of water dry air can absorb at the temperature stated in ounces per 1,000 cubic feet[1]:—

Temperature °C	0	5	10	15	20	25	30	35
,, °F	32	41	50	59	68	77	86	95
Oz. per 1000 c. ft.	4·8	6·7	9·2	12·7	17·1	22·7	30·0	39·2

It would thus seem possible to dry leather by merely increasing the temperature of the surrounding air, but it must be also borne in mind that although dry leather will stand a considerable amount of heat without damage (p. 292), wet goods would suffer serious harm if their temperature were much raised, and hence we see the desirability of using even moderately warm air only in the later stages of the drying. This conclusion is further justified by the fact that the cost of heating air is very considerable compared with the cost of renewing it, but in drying out goods completely some heat is usually necessary to remove the last traces of the excess moisture, as these are somewhat obstinately retained by the leather fibres, and the process can be kept economical by afterwards using this partially wetted and cooled air for the goods in the earlier stages of drying. It should be remembered, also, that the evaporation of water from the leather consumes the same amount of heat as the evaporation at boiling point, and as this heat is obtained from the surroundings, the vaporisation involves a reduction in the temperature of the air and of the wet hides or skins, and hence also a decrease in the capacity of the air for taking up further moisture, so that if the volume of air supplied is not very largely increased, the employment of a certain amount of heat is necessary.

The drying power of air and the amount of moisture it already contains is best determined by means of the wet and dry buib thermometers. This device consists of two

[1] Practically identical with grams per c. metre.

thermometers, one of which has its bulb covered with muslin, kept wet by attaching to it a piece of lampwick which dips into a small vessel containing distilled water. The instrument is placed in a draught, and the water which evaporates from the wet bulb causes a reduction in temperature proportional to the amount of evaporation. This evaporation will be greatest when the air is driest, and the difference between the readings of the two thermometers is therefore a measure of the drying power of the air. In practice the most suitable difference between the two readings should be ascertained for the particular class of goods under treatment, and the system of ventilation and heating arranged so as to give always this same difference. The difference between the two readings multiplied by 0·35 for the Fahrenheit scale, or by 0·64 for the Centigrade scale, and subtracted from the total capacity for moisture at the temperature of the *wet* bulb, as shown in the above table, gives the amount of aqueous vapour in the air in ounces per 1,000 cubic feet.

It will be now necessary to outline briefly some of the various systems suggested for the heating of air and ventilation of rooms used in leather drying. In making any arrangements of this nature it is advisable to estimate as far as possible the amounts of heat and air which will probably be required, the essential basis of the calculation being the weight of water to be evaporated in a given time. In this connection it must be borne in mind that decidedly more air must be provided than on the assumption that each portion is wet by the leather to saturation, and also that arrangements must be made to cope with the most unfavourable atmospheric conditions, with some further allowance for accidental circumstances.

Weather drying, or drying under the prevailing atmospheric conditions, is often useful for drying goods out after tanning or in the earlier stages of drying. If done under cover, the drying loft is fitted with louvre boards, which admit the fresh air from outside which is to replace that already used. In this country the method is exceedingly slow, especially in damp weather, and it is also apt to be very unreliable. Steam pipes are often laid in the middle of the floor of such lofts, and the amount of ventilation can be controlled by means of

the louvre boards. Although water vapour is lighter than air, damp air is heavier than dry because of the contraction caused by cooling due to evaporation. Hence, if the pipes are on the floor, the hot air rises, and a certain amount of circulation would occur even if no other means of ventilation were provided.

Screw-fan ventilation is now largely resorted to for circulation of air in leather drying, the air being heated by passing over a coil of steam pipes. These fans are suitable for moving large quantities of air at a small velocity against little resistance, and are arranged to *suck* rather than blow the air along the drying room, as a more uniform current is produced in that way. The leather should be hung edgeways to the current in order to allow a thorough and constant change of air, and any gangways should be closed up at intervals by partitions. This system is of course inapplicable to a room fitted with louvre boards, and must be used in a room in which the source of the air is at the opposite end to the fan. It is clear also that several small fans will produce a more even current than one large fan. In many cases it is advantageous with this system to arrange a circulation of the air through two rooms, either vertically above each other or on the same floor. These rooms should be fitted with openings at each end and air valves, in order to have facilities for the admission and exit of air, as may be desired.

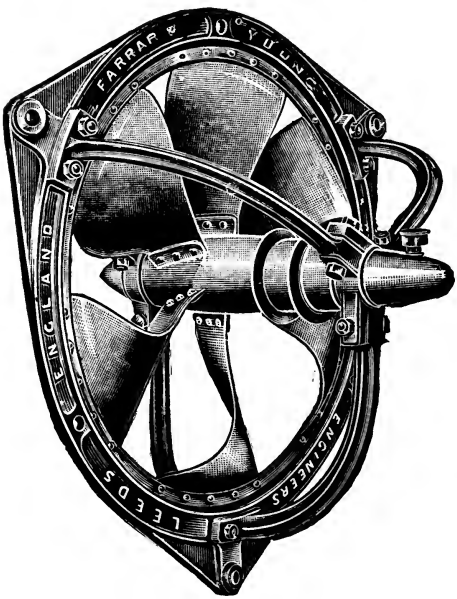


FIG. 60.—Screw fan.

Centrifugal fan ventilation is well illustrated in the system of the Sturtevant Fan Co. In this method the fan blower passes the air over two groups of steam pipes. The first group merely warms the outside air up to about 15° C. and delivers it then to the second and main heater. The air may pass through or over this heater, and an arrangement of dampers allows the hot air and merely warmed air to be blended to any desired temperature. The air is then conducted by means of pipes to the drying rooms where it is thoroughly distributed by means of branch pipes and discharged close to the floor. It then rises and passes between the wet goods and is discharged through wall flues above the roof. These outlets, however, may be closed and the air caused to pass through a return duct from which it passes again through the tempering steam coil along with fresh air, and thence to the fan.

Many other forms of the blast system have been suggested, such as that of Messrs. F. Hattersley, Pickard & Co., in which case a screw fan blows the air through coils of steam pipes and afterwards delivers it to the drying rooms by pipes placed round the bottom of the walls of the building.

Downward ventilation has also been applied to leather drying. When warm dry air is admitted at the bottom of the drying room, it becomes damp and heavy (because of cooling) on rising between the wet goods, and there is therefore a considerable tendency to form local upward and downward currents and hence irregular degrees of saturation and drying, but in the system of downward ventilation the warm air is admitted at the top and the outlets are all at the bottom, and no mixing occurs with the damp, heavy air which is uniformly pressed down and out of the room. The steam pipes are placed in a partitioned space near the wall, the air being admitted from the outside at the bottom of this space and admitted to the room at the top. To obtain a good circulation, however, it is necessary to use a fan either to blow in the air at the top or suck it out from the bottom.

Turret drying is worked on the principle of the chimney. A seven- or eight- storied building is fitted with steam piping at the bottom where the air is admitted. The air becomes heated and light, and rises up through the various latticed floors of

the building. This method, however, requires both a high shaft and a considerable difference in temperature to give a good draught, and although employed in America with some success it is quite unsuitable in this country.

Stove drying is only used in finishing off the drying process or in removing small amounts of superficial moisture, as in morocco finishing. It involves the use of dry air at a fairly high temperature and with little or no ventilation. The stove is heated by steam pipes running right round the room, or by a coil in the centre.

Samming is an exceedingly important operation by which leather is brought into a uniformly half-dry condition, this state being quite necessary for many of the finishing operations, *e.g.*, setting, striking out, shaving, splitting, stuffing, fat-liquoring, staking, embossing, graining, etc. The "sammed" condition may be obtained in three ways—by drying out completely and then wetting back by dipping through water (often tepid) and leaving "in pile" for some hours; by drying the wet goods in suspension to the required consistency and no further, wetting back any parts that have become drier than the bulk and leaving in pile for a time to become uniform; and by machine samming, in which case the superfluous moisture is removed by the pressure of machine rollers. There are three types of samming machine—in one the pressure is by rubber-covered rollers, in another by a sectional metal roller, and in a third the leather is first "set out" (p. 285) by means of a spiral knife-blade cylinder. All these machines are useful in removing the excess moisture in and on the leather and in producing a uniformly damp condition, but none of them dry the goods quite sufficiently for any of the above-mentioned operations, and hence it is necessary usually to hang up for a short time for further drying. Screw presses and hydraulic presses and centrifugal force have also been used for the removal of moisture from leather, but are not widely employed in this country.

It may not be out of place here to outline the methods usually employed for drying the principal varieties of leather. Sole leather is gradually dried out as far as possible by ordinary air, heat being only used in the last stages of the

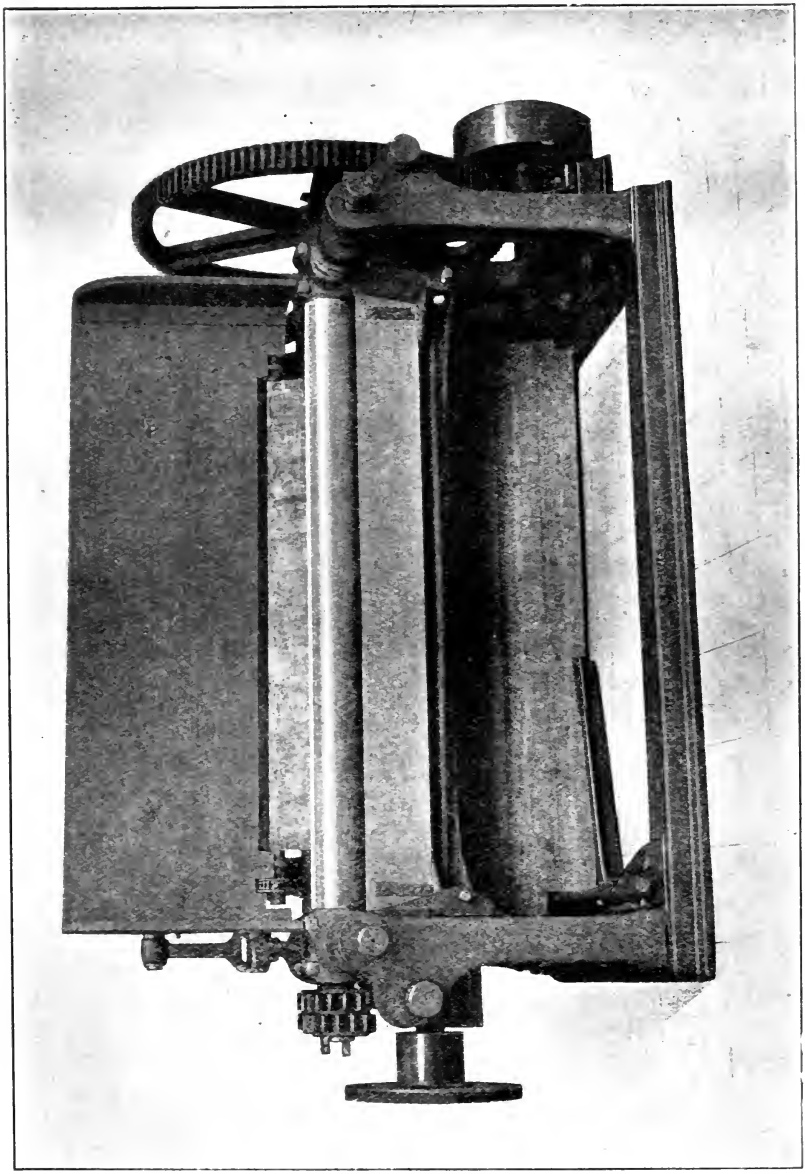


FIG. 61.—Samming machine.

drying. Dressing leather is often weather-dried out of tan and sammed for shaving by wetting back, but it is in some cases sammed out of tan and wet back only where necessary. It is sammed for stuffing by suspension, but is now often passed through a samming machine. After hand-stuffing it is dried at moderate heat—sufficient to keep the fat in a proper state of fusion—but slowly, and therefore with little ventilation. Light leathers are almost invariably dried out completely, and in that condition are sorted according to size and quality. This is known as the "crust" state. They are then wet back for the finishing processes. Dyed leathers are dried fairly quickly, so that the dye may not sink in, and the final drying of this class of leather is often in the stove. Chrome leather dried out thoroughly just after tanning will not wet back again, and in consequence the valuable "crust" stage does not exist for this class of leather. It is dried out completely, however, after fat-liquoring, and sammed by putting overnight in damp sawdust. Alumed leathers must be dried out quickly, but the appropriate temperature varies with the nature of the goods.

CHAPTER XXI

THE FINISHING OF SOLE LEATHER

THE finishing of modern sole leather has for its aim the production of a firm leather which has a clean smooth grain and a light even colour, and which is not brittle. As hide substance is by far the most expensive part of the material which goes to form the leather, and as sole leather is usually sold by weight, the aim of a profitable tannage is to get into the hide the maximum amount of tannin, bloom, reds, etc., and in the finishing processes to obtain the qualities mentioned above with as little loss in weight as possible. An outline of the finishing of the principal varieties of sole leather will now be given, but, as in all processes, the exact treatment differs considerably in different yards.

Butts from a Mixed Tannage which are to be made into "scoured bends" are laid in pile to drip for 2 or 3 days on coming up from the last layer liquor. This is found to render some of the "loose" tan of the interior less liable to be removed in the later processes, and allows the goods to firm up somewhat. The butts are then often rinsed through strong liquor to remove the more loose solid material, and possibly brushed on the grain. After piling again for a short time they are **scoured.** In this process the grain side, after wetting, is worked with stone and brush, and the uncombined tannin and the bloom thereby removed from the grain surface. If this were not done the former would cause bad colour and the latter unevenness of surface, but by their removal a considerable amount of 'weight" is lost. The scouring is now almost universally done by machine, the Wilson machines being the most generally used. Either the six-arm scourer (Fig. 62) or the four-arm butt "striker," fitted with stones and brushes (Fig. 63), may be employed. In the latter the butts pass through the machine over a slowly rotating cylinder and the

tools are caused to work upon the grain, which is wetted by means of a damp cloth. The amount of bloom, etc., removed

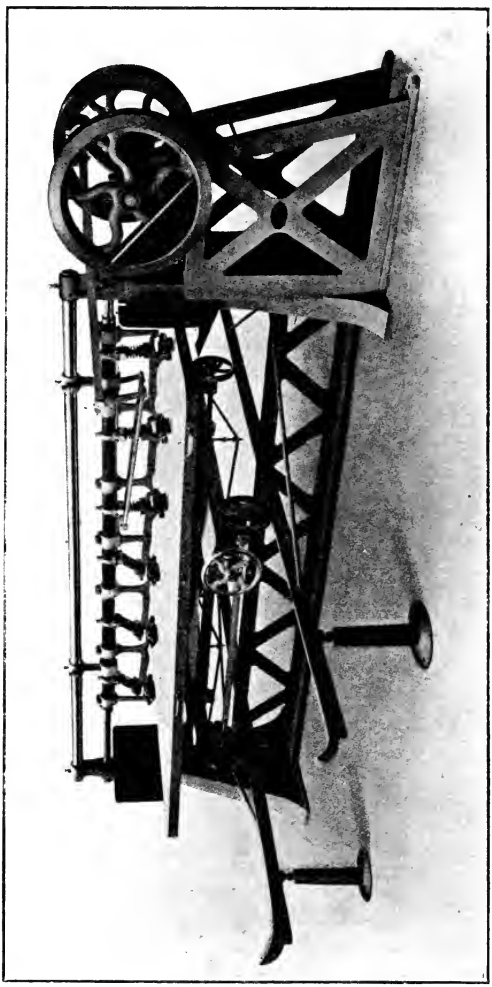


FIG. 62.—Wilson six-arm butt scourer.

from the goods depends upon the amount of water employed, the angle of the stones, and the pressure that is applied. The butts are put through at least three times, and usually four, twice from neck to butt and twice from belly to belly. The

Turner drum machine (Fig. 22, p. 68) also gives good results. As the goods are received from the machine they are wiped over with a cloth and piled grain to grain and flesh

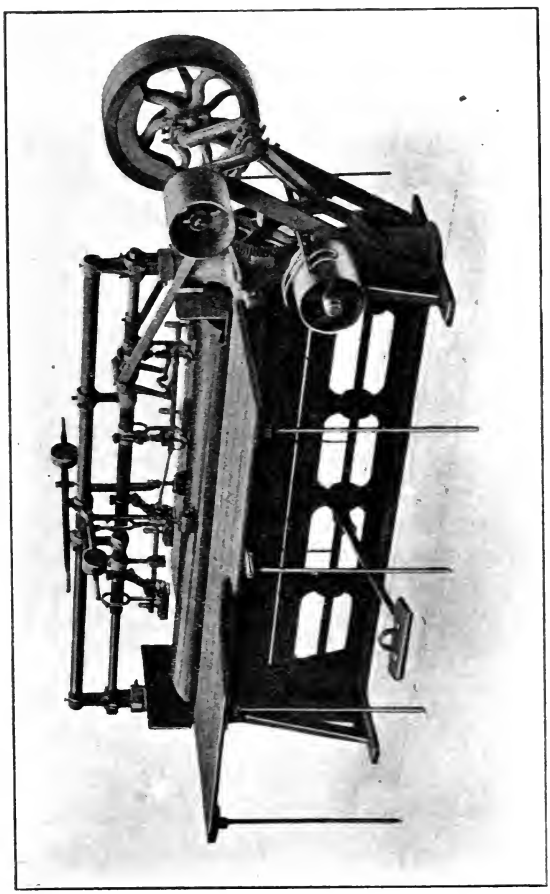


Fig. 63.—Wilson butt striker.

to flesh. This process not only removes bloom, etc., but also assists in laying the grain flat.

The goods now go into the vats. In these they are bleached to some extent by the action of sumach, and a certain amount of weight is restored by means of extract. The precise mode of procedure, however, at this stage varies in different yards

to a considerable extent. If one vat is employed it is made up from a 40—50° Bkr. liquor from the leaches, and with the addition of sumach and a few casks of a chestnut extract of good colour. The vat liquor is kept warm, and the goods go in at 100° F. and 80° Bkr., and are left overnight. They are then hauled, and if firm may go back for another 24 hours, the liquor being again raised to 100° F. They are then hauled, rinsed, wiped, and piled (or horsed) to drain for 2 to 3 days. The vat should be made up once a month and strengthened in the meanwhile by sumach and chestnut extract. Sometimes more than one vat is employed; for example, the goods may be placed overnight in a 100° Bkr. liquor made up from the best leach liquor and chestnut extract, and then for 24 hours into a liquor in which a certain amount of sumach is employed, and finally rinsed through a hot sumach liquor, all vats being at 100° F. In some yards the butts go through a liquor of oakwood extract and sumach. In other cases special "bleaching extracts" (myrobalans, sulphited quebracho, etc.) are used; the latter type of extract acts by virtue of the excess of sulphites that it always contains, but if afterwards run to the yard it must be carefully blended, or bad weight and colour may result.

After draining, the butts are now oiled into the sheds. They are wiped over the grain with a damp cloth, and then thoroughly and evenly with cod oil, and hung up in the sheds to samm. The principle of oiling in the drying process is that it causes the evaporation to take place largely on the flesh side, and prevents both the egress and oxidation on the grain side of the dark coloured liquor of the interior. If no oiling were given and the drying took place equally on both sides of the butt this liquor would be drawn to the grain surface by capillarity, and there dry to a dark-coloured deposit which would become still darker by oxidation. Ordinarily the oil is gradually sucked into the interior as the drying proceeds, taking the place of the moisture which evaporates. This first drying should be very slowly and carefully done in a dark, damp shed, over a period of several days; the exact length is very variable, being determined by the state of the atmosphere and the arrangements of the shed. The goods may be hung on hooks

or folded over poles. If the former is employed the drying is not uniform, being more thorough at the top; this may be overcome by reversing the ends from which the butts are hung. If the goods are pole-dried a more uniform and rather quicker drying may be generally obtained, but there is a great liability to "pole marks," which can only be overcome by very frequently shifting the position of the goods, especially when somewhat dry. This drying is continued until an indiarubbery consistency is obtained and the goods have just a slimy feel on the grain. If some parts (*e.g.*, the edges) are distinctly drier than the rest, they must be wet back and the goods left in pile for a time to "temper," *i.e.*, for the moisture to become equally distributed.

The butts are now **struck out**, "set out," or "pinned." This may be done by hand labour with a "pin"—a two-handled tool with a triangular section, but is now usually brought about by the Wilson machines (Figs. 62 and 63), fitted with brass slickers, through which the goods are put twice. The slickers are rather apt to leave their marks on the goods in such a way that they are visible when the goods are dried out. To obviate this, the goods are sometimes put through a Turner drum machine with a suitable cylinder; this usually removes all slicker marks, but is liable to leave a mark of its own where the butt has been clamped. The drum machine is also used alone. In any case the goods are carefully gone over by hand after striking, and any obstinate bloom, dirt, etc., washed, brushed or pinned out.

The butts are then wiped, re-oiled, and again hung up in **the sheds** for further drying. Sometimes linseed oil or a mixture of linseed or cod oil is used at this stage, and occasionally mineral oil is added. The drying is very carefully watched and should be regular and gradual. When the goods receive this second oiling they are often mopped over on the flesh side also with a very thin paste of bloom obtained from the scouring machines, care being taken not to put it on the grain. This gives some weight and improves the appearance of the flesh on the finished goods.

After 2 or 3 days the goods are in an even damp condition, and are now ready for **rolling on**, after tempering where

necessary. This was once done by a weighted box supported on a smooth brass roller, but is now done universally by

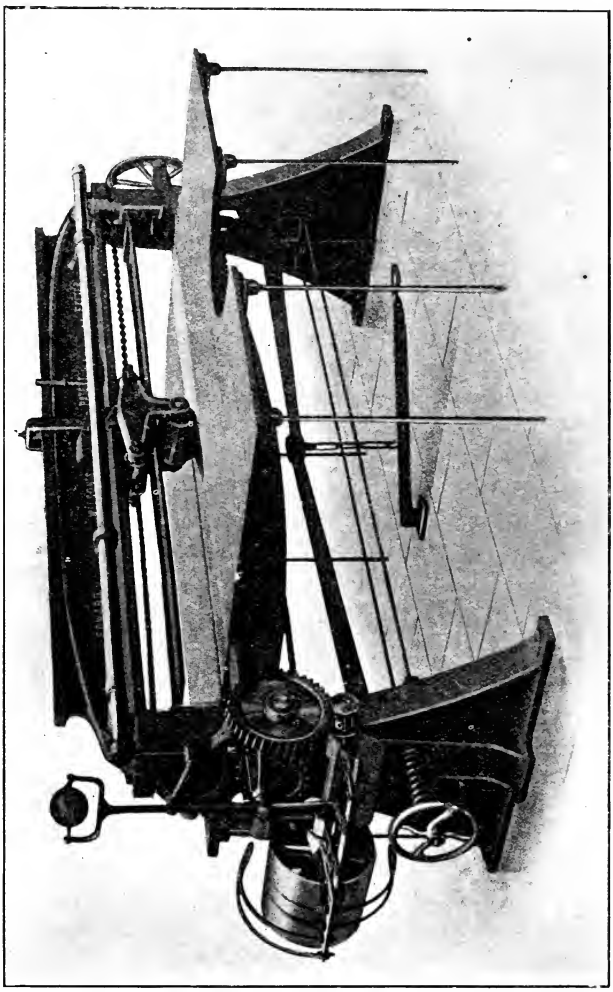


FIG. 64.—Wilson's single-bed butt roller.

machines. This rolling should be rather light, and may be quite effectively done by the old-fashioned dead-weight roller, the butts being put through twice, from neck to butt and from belly to belly. Wilson's single-bed or twin-bed butt rollers

(Figs. 64 and 65) are also quite excellent for this rolling. The goods are now dried further, until the grain is nearly dry and the light colour begins to appear. They are then rolled off with

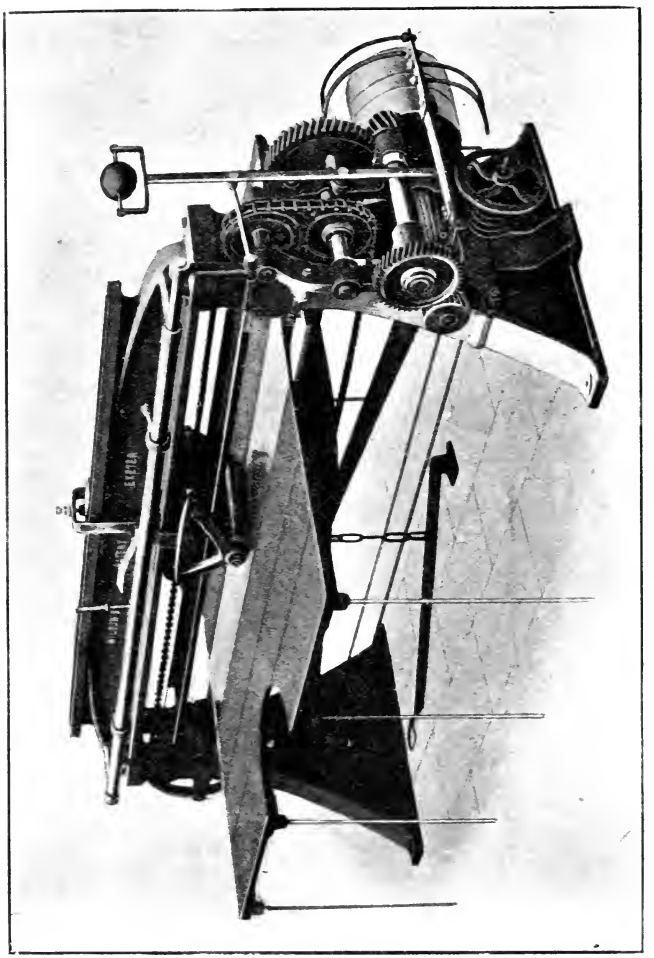


FIG. 65.—Wilson's twin-bed butt roller.

heavy pressure in the Wilson machine, after being tempered only on the flesh side. Both rollings have for their object the production of firmness and of smooth and even grain. The drying is now completed rapidly in the "stove," in which

heat is nearly always employed, the last traces of moisture being held with greater tenacity. The goods are now a light, even colour, and are finally polished by brushing, generally by machine (Fig. 66), and passed on to the warehouse, where they are sorted according to their weight and quality. Brushing is sometimes done before rolling to prevent dirt

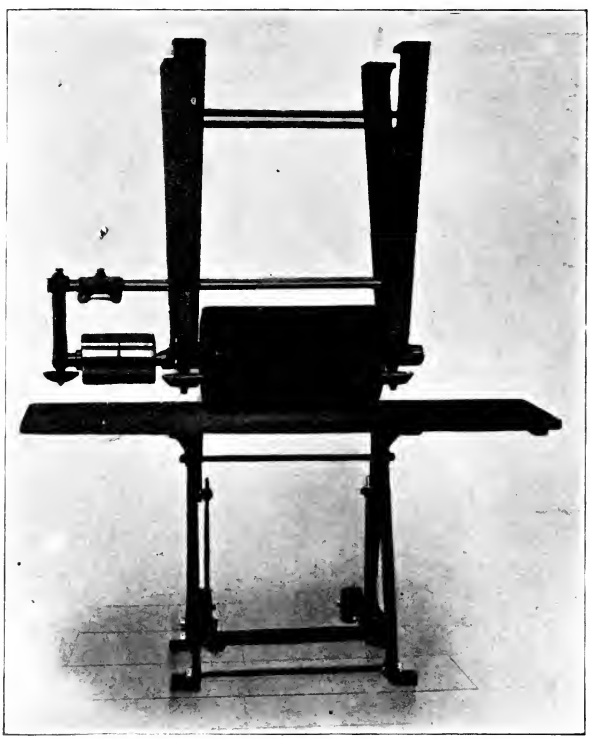


Fig. 66.—Brushing machine.

being rolled into the leather. The butts are also cut up, usually down the middle of the back, into two equal "bends," sometimes before rolling on, sometimes before rolling off, and sometimes in the warehouse.

The shoulders are often drum-scoured. On coming from the last layer they are allowed to drip for some time, and then put into a drum capable of revolving at 6 to 8 revolutions per

minute, and containing sumach made into a thick paste with some bright chesnut or bleaching extract. They are drummed 1 to 3 hours. The friction scours out the bloom, the extract keeps up the weight, and the sumach bleaches. Some drum in extract only, and some in sumach and sumach liquor only. After drum scouring the goods pass through a sumach vat at 30—40° Bkr. and 100° F. They are afterwards drained, oiled, and hung up in the sheds to samm, and are then pinned or

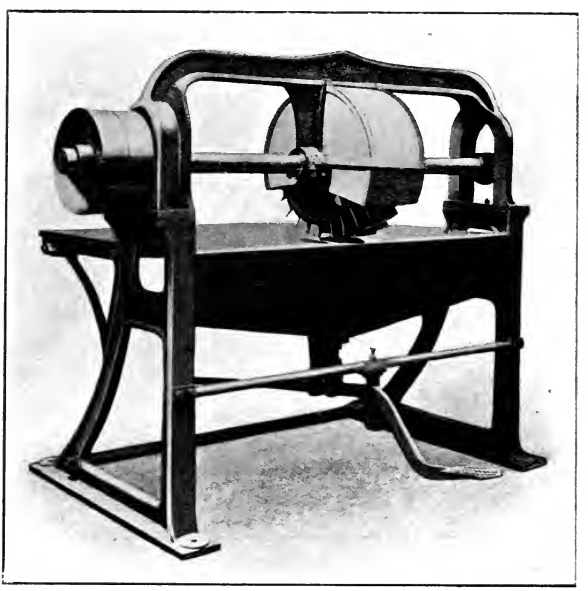


FIG. 67.—Priestman striker.

struck out in the Priestman striker or "slugger" (Fig. 67), which takes out creases and stretches the goods. They are oiled again into the sheds, and dried off and rolled just as for the butts.

The bellies are also drum-scoured, horsed to drain, oiled, sammed, and struck out in the "slugger." If for split work they are put through the band-knife machine (p. 281) at this stage, being kept fairly damp and well tempered. They are finished off as usual. Both shoulders and bellies are often

drum-oiled after striking, and care has always to be taken with offal to wet back and temper well before each mechanical operation. Special rollers are generally used, such as that of Wilson (Fig. 68)

Butts from a West of England Tannage are very heavily bloomed on account of the large proportion of valonia which is used in the tannage, and no attempt is made to remove this completely as in the case of an ordinary mixed tannage; hence the goods are finished off as "bloomed butts." On coming from the last layer they are laid in pile for 3 or 4 days,

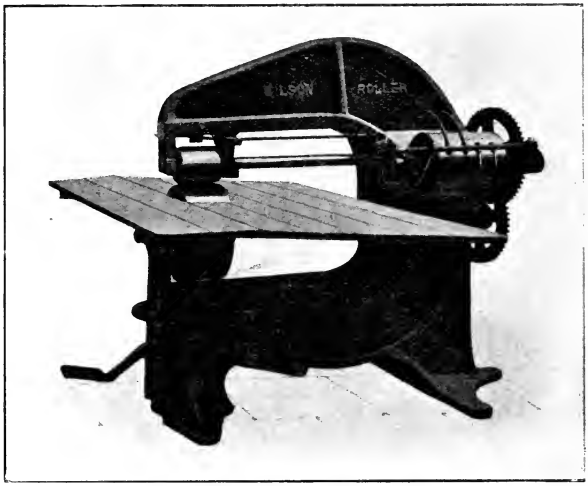


FIG. 68.—Offal roller.

then rinsed through a 50° Bkr. clear liquor and laid on a sloping bed over a pit, where they are brushed with a broom to remove particles of valonia, etc. The butts are now horsed or hung up for a few days to **dry partly**, sometimes being lightly oiled. This drying must be done slowly and in dark sheds. They are now piled to **sweat** for about 3 days on a covered floor until a white mould begins to form. They are now ready for **scouring** with the Wilson machine, being wet on the grain with soap and water, and occasionally a little oil. This process, being carried out in a much drier condition than described previously, merely removes the surface bloom and

lays the grain somewhat. A blunter tool is also used than for scoured bends, and where the pin is used it should be held so as to force the bloom into the leather rather than bring it out. The goods are then wiped over, oiled, sammed, hand-pinned where necessary, wiped, re-oiled and dried till ready for **rolling on.** After rolling on, the goods are coloured with a mixture of ochre, French chalk, size and oil, which mixture is well rubbed in and smoothed over with a cloth. They are then brushed to polish, rolled off, rapidly dried out, and finally brushed again. In some yards the butts are coloured, after pinning, with aniline dyes and other staining mixtures, and are sometimes scoured rather more thoroughly both by machine and by hand.

This method of finish is decidedly cheaper, gives better weight, and does not give a result widely different in appearance from clean scoured goods. The offal is finished off in a manner very similar to the butts.

Butts from an Oak Bark Tannage, on coming from the last layer, are rinsed through a clear 30° Bkr. liquor and allowed to drip 2 days. They are then oiled into the sheds, slowly dried for a few days, and piled to heat. They are then scoured, pinned, wiped over with warm water, oiled, hung up to dry further, stretched, re-oiled and dried for rolling on, dried out until the colour comes up, and rolled off as usual. The offal is treated very similarly.

American Hemlock Sides are bleached in finishing, and much of the so-called "oak leather" is tanned chiefly with hemlock and the colour merely got up with oak. The goods on coming from the last layer are washed through a clear 40° Bkr. liquor and then **bleached**; they are first placed for ¼ hour into a ½ per cent. solution of borax or soda, which is slightly warm, and then into a warm 1 per cent. solution of lactic, sulphuric or other acid, also for ¼ hour, and finally into cold water for another ¼ hour. They are then laid in pile for a time, oiled off and dried out completely. **Oiling** is often done in drum and even in pit, but where **weighting** is practised the goods may be sammed by machine oiled on the grain and coated on the flesh and often on the grain with a strong solution of 70 parts glucose and 30 parts Epsom salts (magnesium

sulphate). About 10 per cent. of this mixture can be used on the weight of the leather. Glauber's salt (sodium sulphate)

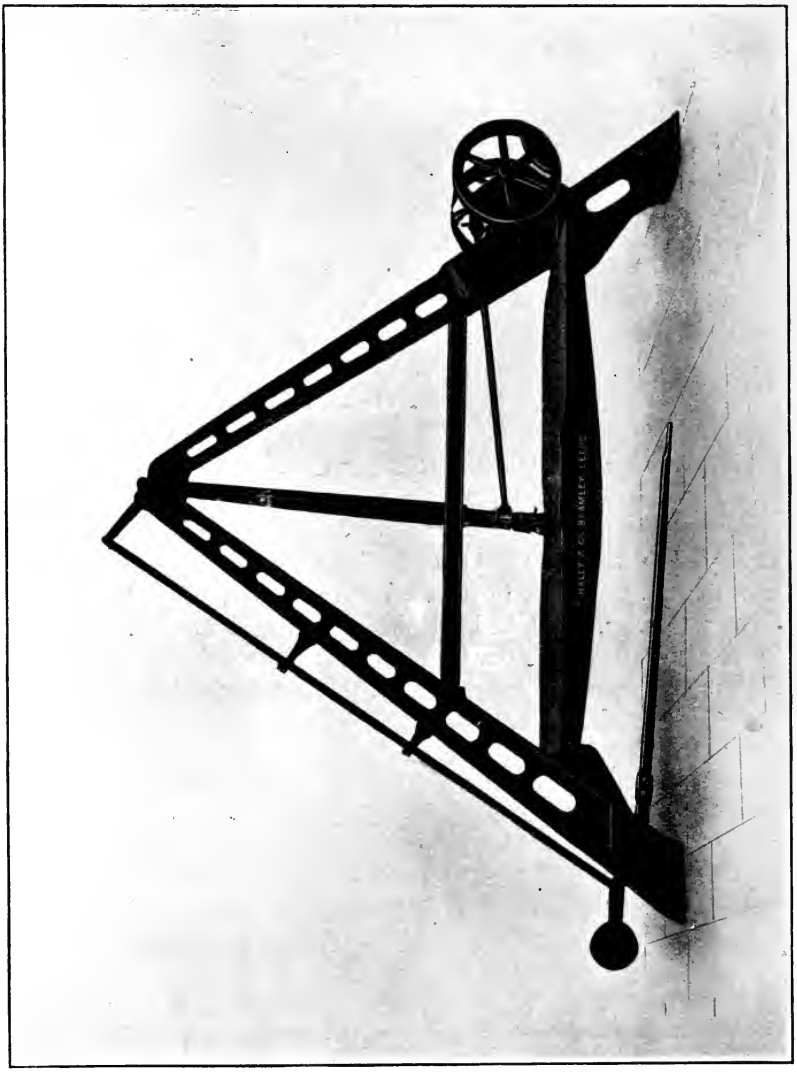


FIG. 69.—Pendulum roller.

may replace the magnesium sulphate. The goods are dried out completely. It will be noticed that there is no scouring

or striking, for with American sole leather there is no bloom to remove. The goods are damped back for finishing and tempered; this is done by brushing over the grain with a wet brush and leaving in pile overnight. Next morning they are heavily rolled with a rapidly-moving pendulum roller, which polishes as well as smoothes the leather.

Drum-Tanned Sole Leather is very apt to give poor weight, even though the goods come finally out of neat extract

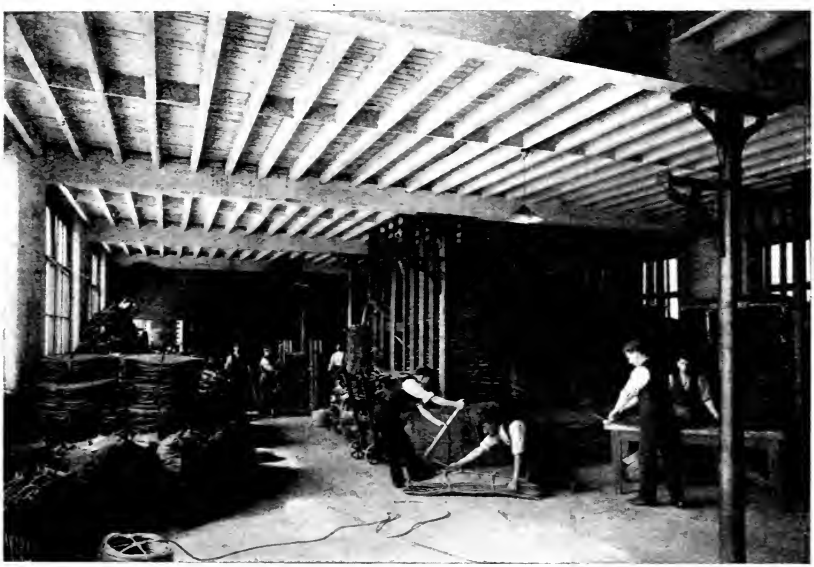


FIG. 70.—Portion of leather warehouse (Messrs. Walker, Ltd., Litherland).

at 25° Bé'. The problem is, therefore, to remove as little extract as possible consistent with good colour. As, moreover the goods are not bloomed, no scouring is usually necessary, but as scouring assists materially in laying the grain flat, its omission gives rise to the necessity for heavy striking machinery. Another point which makes it still more difficult to obtain a smooth grain is that the ordinary "rolling on" cannot be given, for the extract in the interior will be squeezed out. The "rolling off" must therefore be only when the

colour has come up and the grain is dry, and it must be very heavy.

The goods are taken out of the last drum liquor and washed up in an extract liquor at 50° Bkr. for three hours, handling once, and afterwards in water at 25° C. for three hours, also handling once. This cleanses the goods from all surface extract, and the vat liquors in which the goods have been steeped are used in the early drum liquors and the suspender

FIG 71.—Loads of leather leaving tannery (Messrs. Walker, Ltd., Litherland).

liquors. The goods are now oiled somewhat lightly and hung up to samm. They are then heavily struck out, special machines being usually employed. There are now two courses which may be followed. In one of them the goods are re-oiled, dried, further struck out again, lightly oiled again and dried until the water does not show on the grain, wetting back the flesh if necessary on the drier parts, and finally tempering in pile, flesh to flesh and grain to grain; they are now rolled off with heavy pressure, dried out at moderate

heat in the stove, and brushed. In the other method the goods are oiled well after striking and dried out completely They are then wet back by damping on the flesh only and allowing to lay in pile till the water does not show itself, rolled off with very heavy pressure, dried out in the stove, and finished with the brush as usual.

The advantage of drum tannages lies in the saving in time of tanning, in tanning material, and in tanhouse labour (leaching, handling, etc.), but the heavy weight finish is very liable to give poor substance, and there is always some tendency to "pebbly grain" on account of the rapid increase in tannin concentration and the little work in the finish. Further disadvantages of drum-tanned sole leather are the readiness with which it wets back with water and the tendency to spread in wear and go out of shape. If carefully manufactured, however, the tensile strength is usually good.

CHAPTER XXII

THE CURRYING AND FINISHING OF DRESSING LEATHER

The methods employed for the finishing of goods tanned for belting, harness and upper leather, etc., consist of very varied and largely mechanical operations, of which the most essential process is that of "stuffing" the goods with oils and fats, thus rendering them pliable and waterproof. Most of the other operations are either preparations for this particular operation, or processes for improving the quality and appearance of the finished goods. These processes, which are known as "currying," will now be briefly outlined.

Soaking the dried-out goods is usually one of the first operations to be carried out in order to prepare them for the subsequent processes of shaving or splitting. This is done by steeping the goods for a few seconds in a tub of water, often warmed up to about 40° C., and afterwards laying them "in pile" or horsing them up for some hours until thoroughly and evenly damp. For splitting it is very important that there should be a complete absence of creases or folds, and hence the goods after samming in the above way are often "jacked" with a stone or by a machine somewhat resembling the inclined bed glazing machine (Fig. 101, p. 341). Foreign-tanned kips are often drummed after soaking, both to soften the goods and to effect the removal of any extraneous matter. Sometimes goods are thoroughly wet back by prolonged steeping or drumming, and afterwards hung up to dry to a suitable condition.

Shaving comprises a reduction in the substance of the leather on the flesh side by means of suitable sharp knives, with a view to rendering the thickness uniform and the surface even, which conditions are necessary for the production of a satisfactory finish on the goods and for the purposes for which they are afterwards used. Hand-shaving is the older process, and is a good

example of skilled labour. It is brought about over a beam (Fig. 72) of which the nearly upright part has a smooth wooden or glass face. The goods are placed over this upright part, flesh side up, and shaved down the flat, smooth face with a special currier's knife (Fig. 82) of good steel, the edge of which is exceedingly keen and is *turned*, so that the tool is used with the greater part of the knife almost at right angles to the face of the beam. This wire edge of the knife is extremely

Fig. 72.—Hand-shaving.

delicate, and its keenness needs constant restoration by means of a handled smooth wire with a round end (Fig. 82), which is run both along the groove between the knife and its turned edge, and along the outside of the turned edge. Longer, wider and more sloping beams are used for the heavier leathers (harness backs, etc.), to obviate any obstruction in the work. Heavy goods of this type also shaved on a horizontal table by means of a "shaving-slicker," which, like the shaving-knife, possesses a turned edge. The "buffing slicker"

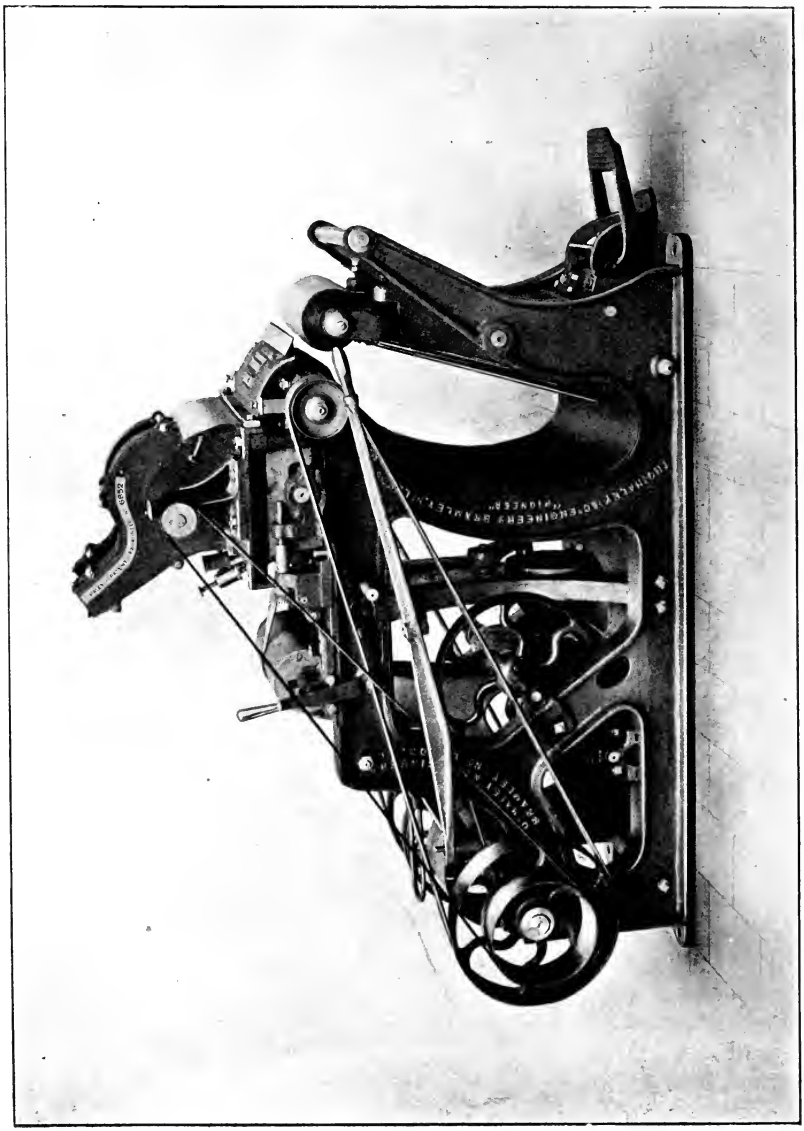


Fig. 73.—Shaving machine.

is another sharp currier's slicker used for removing a thin layer on the grain surface, and the whitening slicker is a somewhat similar tool used for the flesh side in the finishing operations.

Machine-shaving is now extensively employed in place of hand work, and in competent hands is much quicker and more economical. For high-class work, however, it has not yet superseded hand-shaving. The usual type of machine (Fig. 73) essentially consists of two rollers. One of these is for cutting, and is fitted with a spiral knife blade of steel, half of which is a right-handed and half a left-handed spiral, so that the roller will spread whilst it cuts (cp. pp. 70 and 334). The other roller is smooth, and covered with hard rubber composition or nickel-plated metal. The goods are placed over this roller and are brought in contact with the cutting roller by pressing it forward with a foot treadle, the goods being held in the hands. The cutting roller is generally well under cover, and can be sharpened by an emery wheel which is part of the machine. A cylinder-roll with seven blades on both left and right spiral is satisfactory for ordinary shaving; 10 blades on each are required for "flatting," 10 to 14 blades for "whitening," and 18 to 24 blades for "buffing." It is very important for both hand and machine shaving that the leather should be suitably sammed.

Splitting has replaced shaving to a considerable extent in recent years in the dressing of certain classes of leather. In this process the leather is sliced in a plane parallel to the grain surface, so that the "splits" have the same area as the original piece of leather. The operation is carried out by machine, and consists essentially of presenting the leather in a suitably sammed and soft condition to a sharp knife edge, towards which it must be persistently held or pulled on account of its lack of rigidity. It is now common to split many leathers after merely colouring through in the first handlers (see p. 202), as they are then in a plump and suitable condition, and the method permits a cheaper tannage being given to the flesh splits. Many hides and skins also are now split after unhairing and fleshing when they are swollen and plumped with lime, and sometimes after

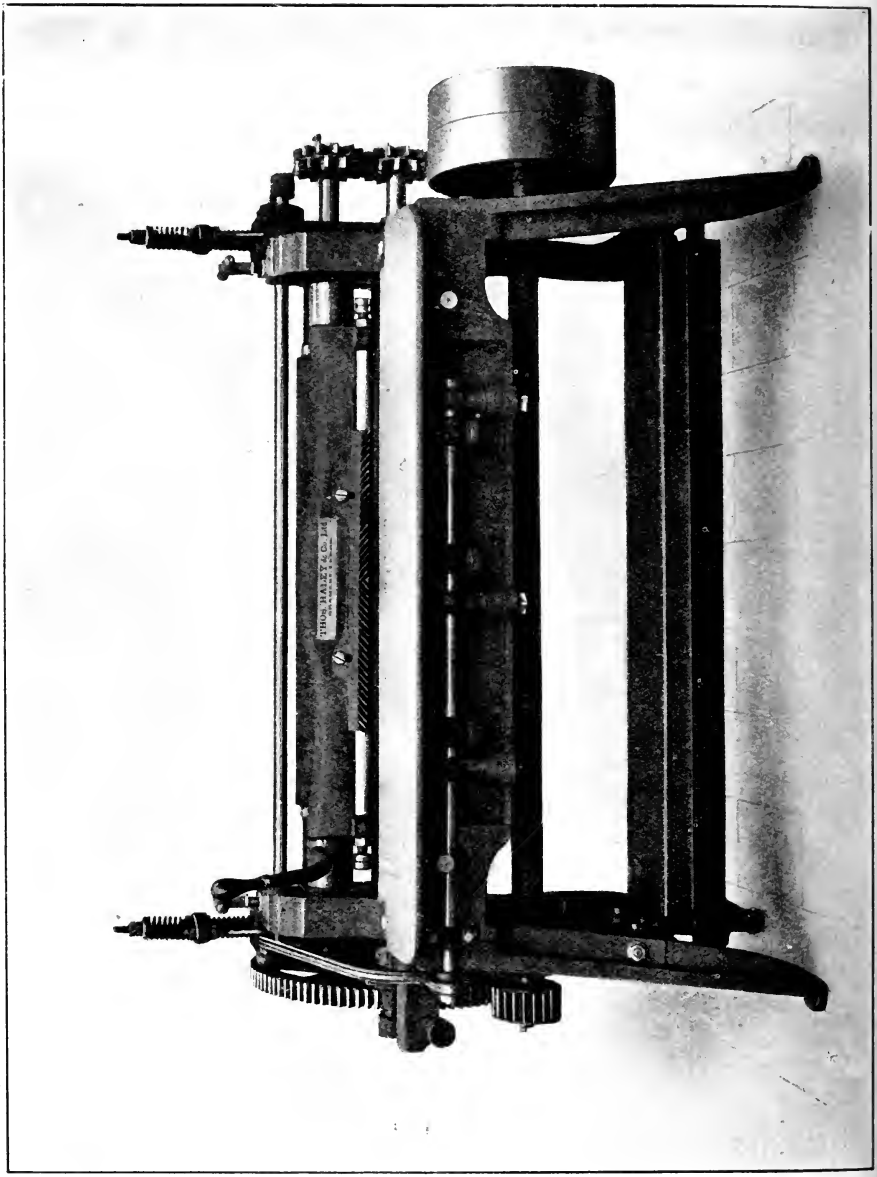


FIG. 74.—Union splitting machine.

drenching, and in these cases a completely different tannage may be given.

There are three types of splitting machine, the "union," the vibrating knife, and the band-knife (or belt-knife) machine. The Union machine (Fig. 74) has a fixed horizontal knife over which the leather is placed grain upwards so that some portion of its area has already passed the edge of the knife. This end of the leather is fastened to a drawing roller about which it is wound by the machine, thus causing the knife to split the rest of the leather. The leather is held in position by means of spring plates and a nipping roller which, by appropriate adjustment, acts also as the gauge of the thickness of the grain. The position of the leather is then reversed, and the portion which has not been split is now drawn to the knife by winding the other part round the drawing roller as before. It is essential for good work that the knife be sharp and keen, and it is therefore necessary to remove it from the machine and rub it with a "clearing stone," and occasionally to grind it. It is clear that with this machine the flesh splits are in two parts; but the machine is nevertheless still considered very suitable for "army butts," "memel butts," etc., as the sliced side of the grain split has a better surface and gives a better finish than is often obtained with the band-knife machine.

In the vibrating-knife (or reciprocating-knife) machine the leather is pulled towards the knife. The knife remains in one position, except that it has in the direction of its edge a small but rapid to and fro motion which is communicated to it by a crank and connecting rod. When the knife is in motion the rollers are stationary, and *vice versâ*, so that a series of cuts are given which can sometimes be detected on the split surfaces. The "grains" and "fleshes" pass forward on opposite sides of the knife, and two whole splits are obtained. The advantage of this machine over the fixed knife machine is that less damage is done by the accidental existence of a notch in the knife edge, a sawing action being then given instead of a rasp or tear. The machine is extensively used for splitting sheep skins in the limed state. Another form of the reciprocating-knife machine is used for splitting green hides. The

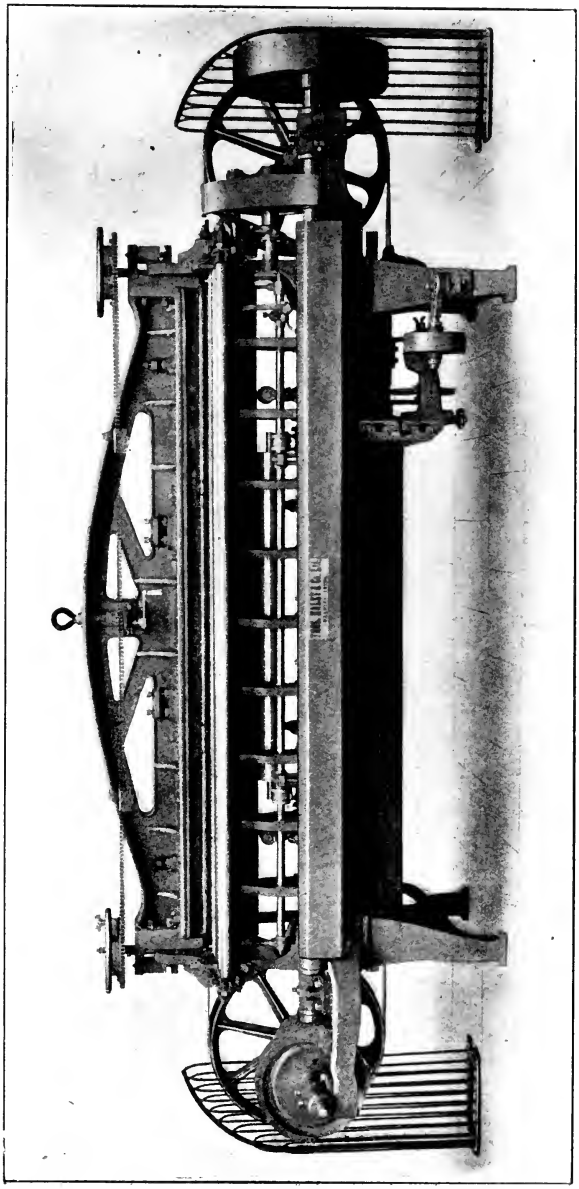


FIG. 75.—Band-knife splitting machine.

goods are placed over a slowly revolving drum, which brings them towards the knife.

The band-knife machine (Fig. 75), which is the most elaborate, and in many respects the most satisfactory, splitting machine, differs from the vibrating knife in that the knife is an endless band or belt which passes round two pulley wheels, being horizontal in the part where it is used for splitting. One of these wheels is attached to power, and by its revolution the "band-knife" is given a continuous motion in one direction. The knife is double bevelled, and the sammed leather is pushed towards it, grain upwards, by two feed rollers; the grain split passes over the knife and the flesh split under it, the former being received by the operator's assistant, and the latter falling to the ground. The knife is kept sharp by emery grinders fixed on the lower part of the machine, and is kept clean by thick felt cleaners. In some machines these operations are carried out whilst the machine is at work, and in this case the work may be continuous throughout the whole day.

The machines are made in various sizes and with different minor attachments, and a good machine is capable of many adjustments according to the class of goods. The thickness of the splits can be varied considerably, down even to $\frac{1}{16}$ inch, and hence for some purposes it is possible to obtain six, or even more, good splits from one hide or skin. The adjustments, however, are a matter of some delicacy, and a certain amount of experience with any one of these machines is necessary before it yields its best work. Other essentials are the use of clean machines, lubricated with light mineral oil, thoroughly and evenly sammed leather, preferably "stoned" or "jacked," and goods carefully sorted, so that those of the same substance and class are treated together, thereby keeping the amount of readjustment at a minimum. Very frequently the first splitting is merely to level the thicker parts, *e.g.*, the mane of stout shoulders. This is termed "skiving," and the levelled goods are then re-jacked and re-split. The band-knife machine is very extensively employed in this country for many classes of goods, and is especially suitable for hide and kip offal. Its use is almost a fine art in America, and

much of the American success in "glove grain," satin and waxed splits is due to clever splitting with this machine.

Scouring is also an important process for many classes of dressing leather as well as for sole leather. Its aim is to remove bloom, loose tan, dirt, etc., from the hides, and it is effected by means of warm water and slickers,[1] stones and brushes, which are worked over the surface of the leather,

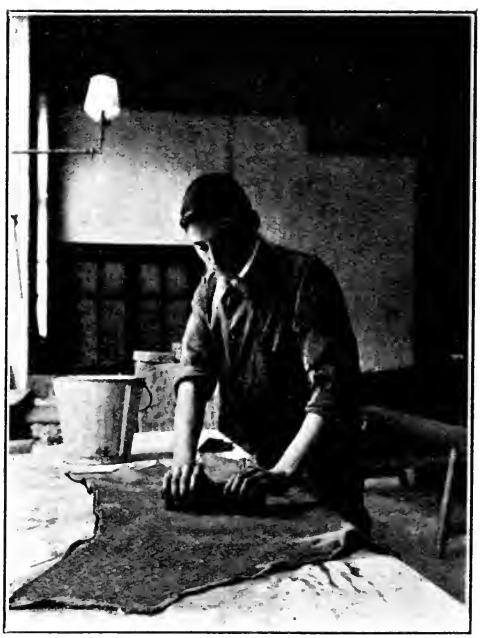


FIG. 76.—Hand-scouring.

often on both grain and flesh. As ellagic acid is soluble in alkalies, the scouring is distinctly assisted by the use of weak soap solutions (0·8 per cent.), and a little borax is also sometimes added. The operation is largely carried out by hand, the slickers and brushes being grasped with both hands. Machine work for this operation is now available, but is often too vigorous for scouring the grain without damage, and is therefore used chiefly for goods that are to be blacked, or for those

[1] Sometimes written *sleekers* or *sleakers*.

which are to be finished on the flesh side. The most generally used machines are the Burdon machine and the Jackson machine. The former (Fig. 77) consists of a sloping table, on which the goods are placed, and a rapidly revolving cylinder fitted with stones and brushes alternately. The table is lifted towards the cylinder with a footboard, and the stones and brushes are thereby caused to play upon the goods. A

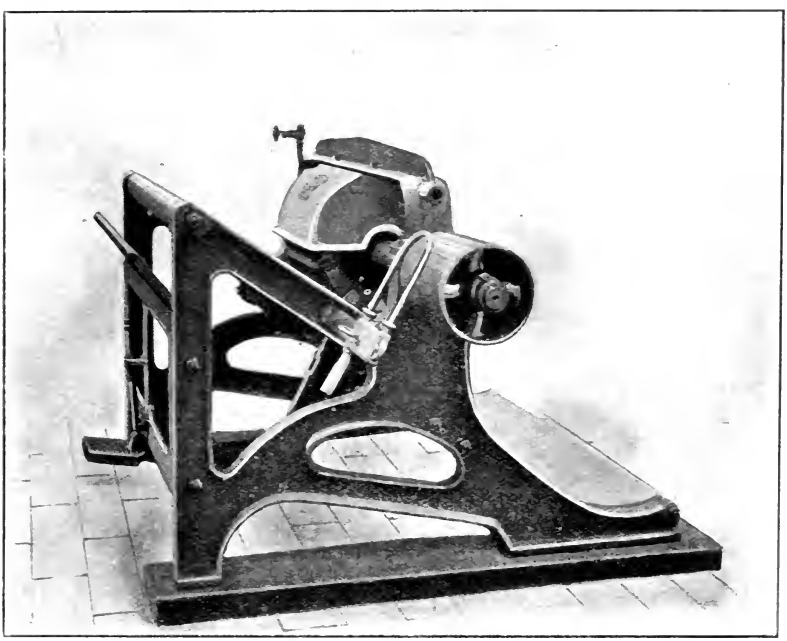


FIG. 77.—Burdon scouring machine (T. Haley & Co.).

modification of this machine (the "Circulum" scourer, Fig. 78), is in use, in which the tools are fixed on an endless band which passes round two pulley wheels, the advantage of this being that the part which works on the goods is moving parallel to the surface of the leather, and hence that the rub is not only less energetic but is also distributed over a larger area. In the Jackson machine (Fig. 79) the machine head possesses a rocking motion as well as a movement

parallel to the leather surface. In all scouring machines the freedom of movement of the table in different directions, and

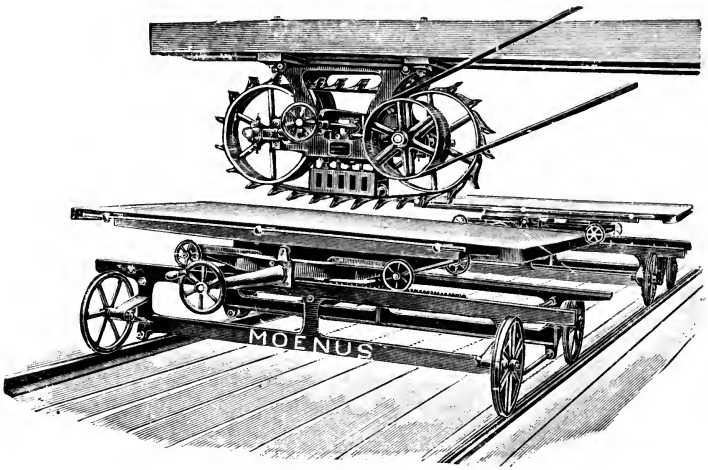


FIG. 78.—Circu'um scouring and butt-striking machine.

the arrangements for raising the table to the machine head, have very great variety with different manufacturers.

The mechanical working of goods by slickers, etc., takes place at various stages in the finishing processes of most

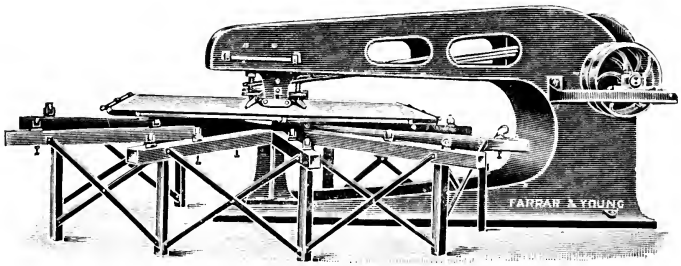


FIG. 79.—Jackson scouring machine.

goods for removing other superfluous matters (moisture, grease, etc.) besides bloom and tan, for getting rid of wrinkles and creases in the goods, and for producing softness and

pliability. It is clear that the tools must be chosen according to the purpose in view, and hence many kinds of slicker are in use, of steel, brass, vulcanite, and slate, and are used in a similar manner to the scouring slickers for "striking out," "setting out," "putting out," "pinning," "jacking," etc.

It is evident also that the Burdon and Jackson machines may be used for some of these purposes by changing the working tools of the machines. Drum-scouring is now common for many classes of goods, the process being quite analogous to that used for sole leather offal, p. 266.

Sumaching is a process which, for dressing goods, often follows scouring, and is somewhat analogous to the vatting or

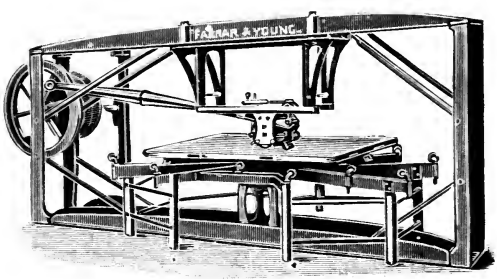


FIG. 80.—Scouring machine.

sumaching of sole leather. Sumach liquors of raised temperature (40—50° C.) are used in which the goods are either handled, paddled or drummed.

Stuffing the goods with oils, fats and waxes is, however, the typical operation for the class of goods now under consideration, and is effected by hand labour, by drumming, and by burning in. The object of the process is to coat the tanned hide fibres with the fats which lubricate them and render the leather somewhat pliable, and also, to a varying extent with different goods, to fill in the spaces between the fibres and thereby give weight and waterproofness. The stuffing of under-tanned leathers has the toughening of the leather also in view, and in many cases a further aldehyde tannage is quite a possibility. The penetration of the oils and fats is more easily brought about than in the case of the oil tannages,

because in tanned leather the fibres are now isolated by the astringent action of the tannins, and the impregnation of the leather is assisted by capillarity. This force alone, however, is quite insufficient, as the surface tension of the oils and fats is too great. Hence the principle of the stuffing operation is to reduce the surface tension of the stuffing materials, and this is effected in two ways: by raising their temperature as

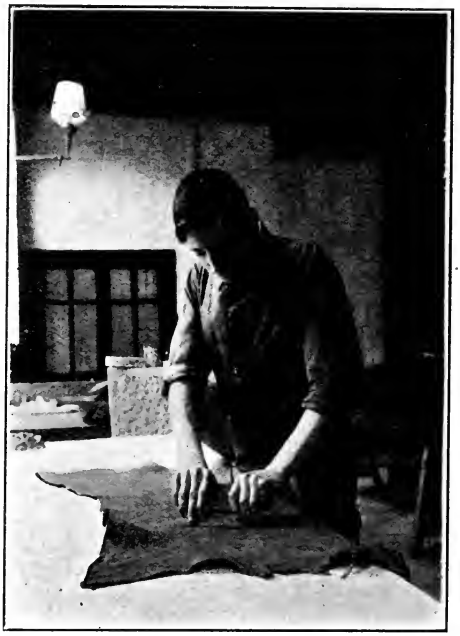


Fig. 81.—Hand-setting.

in the "burning in" process, or by using moist leather, the surface tension between oil and water being less than between oil and air. Emulsification (as in "fat-liquoring," p. 356) is a particular case of the second method, and drum-stuffing is a combination of both methods. It is evident also that oils and fats which have a low surface tension, and which readily emulsify, will be the most readily and most completely absorbed by the leather. The factors, therefore, which determine the "carrying power" of a leather for grease are

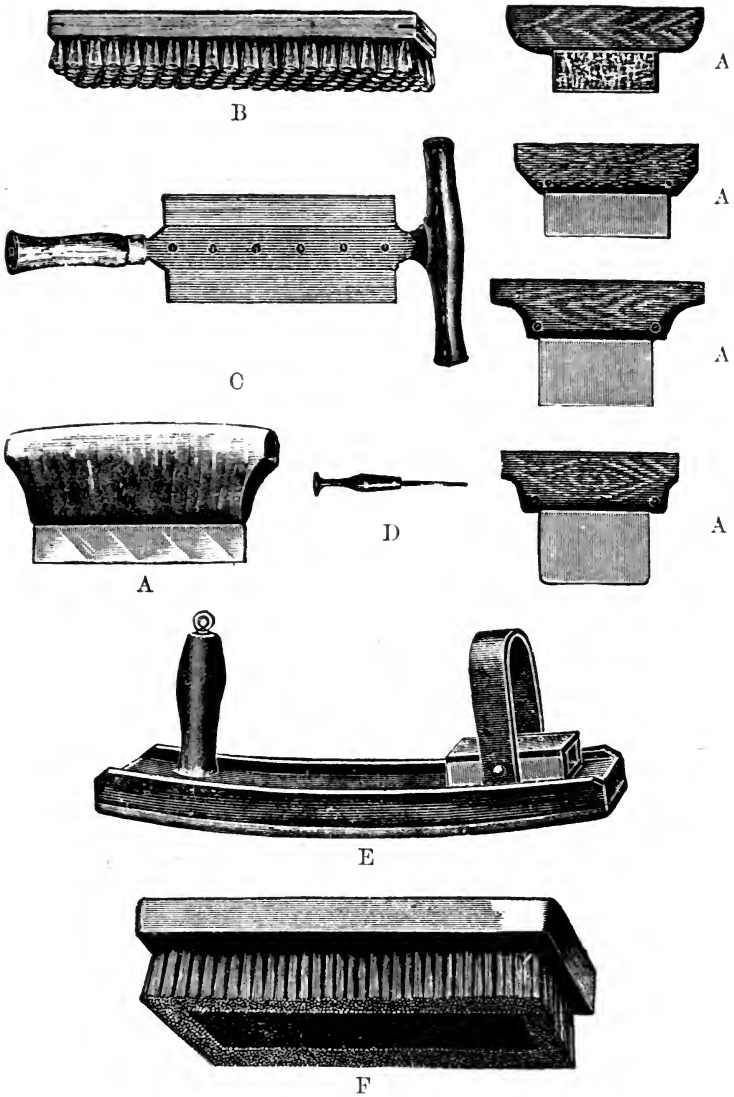


FIG. 82.—Curriers' tools. A, slickers; B, blacking brush; C, shaving knife; D, steel; E, arm board; F, stuffing brush.

the surface tension of the stuffing mixture, the temperature of the materials and operation, and the amount of moisture in the leather, together with the thoroughness of the isolation of the fibres of the hide.

Hand stuffing is the oldest process, and is still used in the dressing of strap butts, harness backs and other high-class or coloured work. In this method the leather is used in a suitably sammed condition, and the flesh side is thickly coated with "dubbin," spreading it with a brush.

The dubbin consists usually of a mixture of tallow and cod oil, which are melted together and cooled with constant stirring, so that as the hard fats crystallise out of the oils in which they have been dissolved they remain in a very finely divided condition, and a creamy and nearly homogeneous salve is obtained. The goods are now hung up in the sheds to dry, and as the moisture evaporates from the spaces between the fibres the oil and soft fats gradually replace it and sink into the leather (cp. p. 262), leaving the hard and solid fats on the outside. These, when scraped off with a slicker, form "table grease," and are often mixed in with soft fats and oil and used over again for stuffing. The proportions of tallow and oil vary with the nature of the leather and also with the condition of the atmosphere and the temperature of drying, a greater proportion of harder constituents being employed for warmer conditions. The stuffing mixture must not be too solid, for it is only the softer parts which enter the leather, and it must not be too liquid or it will run off the leather on to the floor. The tallow, therefore, is useful not only in yielding some of its softer constituents to the leather, but also in making a semi-solid mixture which will adhere to the leather when thickly applied. Other substances, *e.g.*, French chalk (steatite), can fulfil this latter function.

Drum stuffing is a later and quicker process in which the sammed leather is placed in a drum heated to about 60° C. The melted stuffing materials are run into the drum through the hollow axle, and after about half an hour's drumming, or less, they are completely absorbed by the leather. Various kinds of drum are used for this purpose, an ordinary closed drum

being quite workable, but the usual types employed (Figs. 83, 84 and 85) are specially fitted with a steam-jacketed or heated

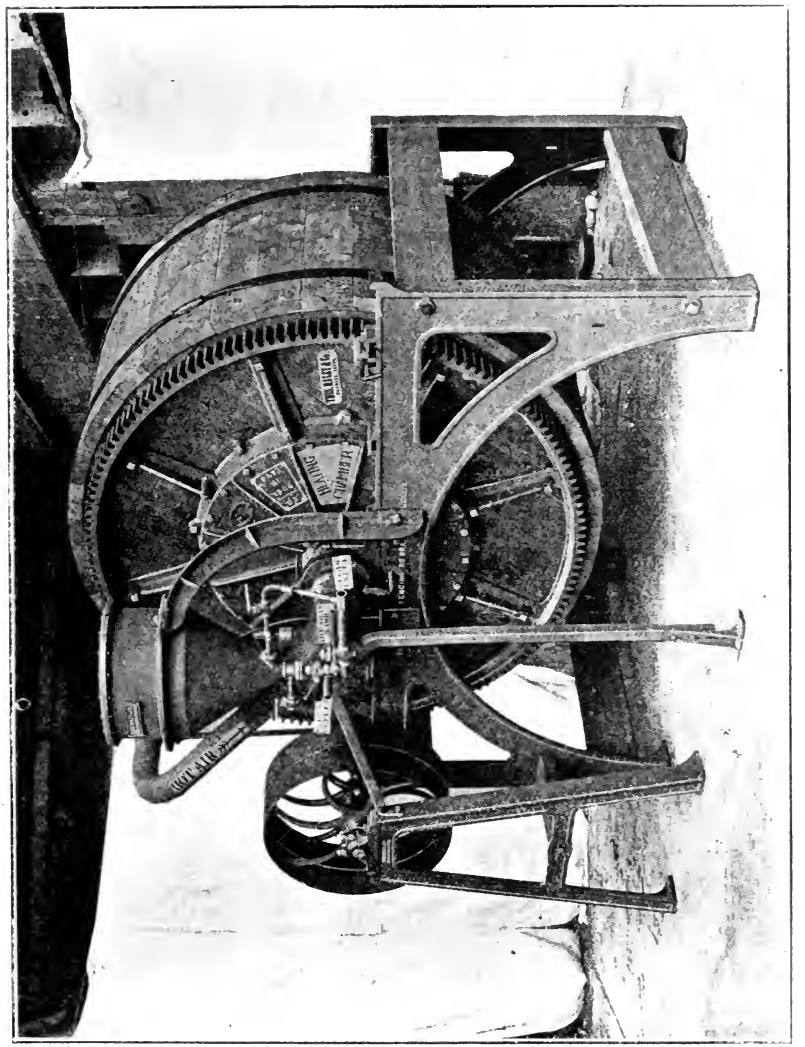


FIG. 83.—Hot air stuffing drum (T. Haley & Co.).

funnel in which to keep the grease melted before it is run through the hollow axle, and a thermometer by which the

temperature of the drum can be ascertained. The steam-heated drum is heated by passing live steam into it through the axle until the required temperature is reached; any water

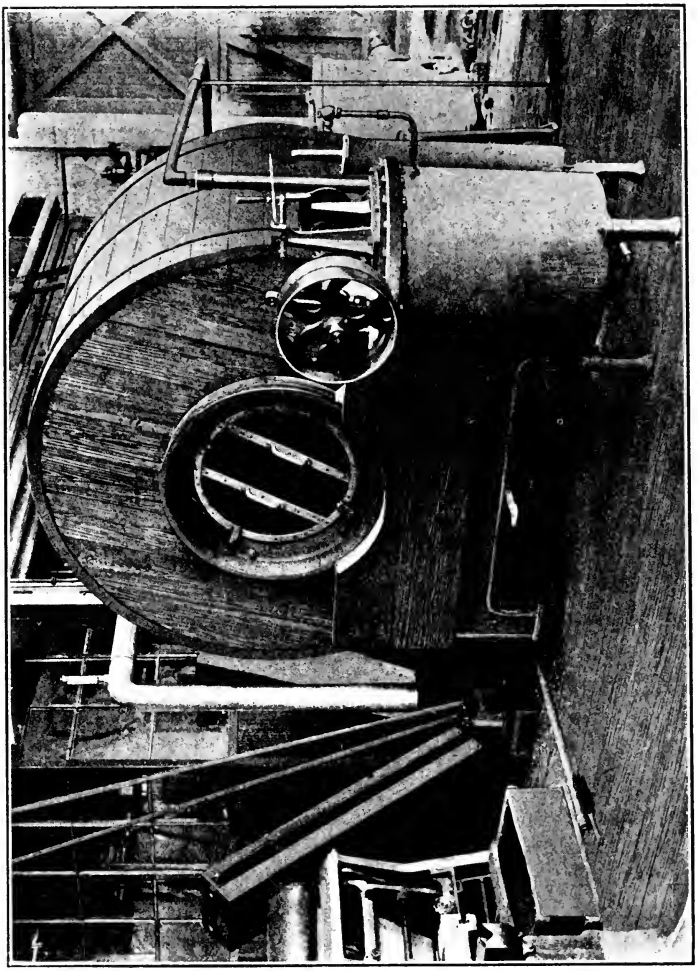


Fig. 84.—Hot air stuffing drum, front view (Farrar & Young).

which has formed is then run off, and the goods are placed inside and drummed dry for a few minutes until they are warmed by the heat of the drum. The melted fats are now run in at a rather higher temperature and the drumming

continued until they are completely absorbed, after which the drumming may be continued, with the door of the drum replaced by a latticed door, until the goods have cooled

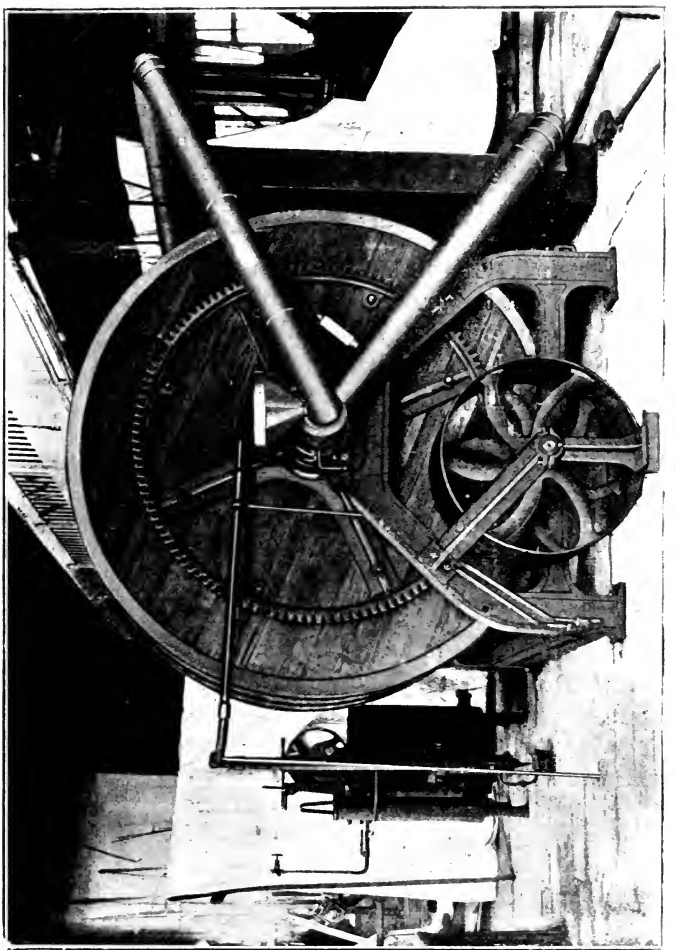


FIG. 85.—Hot air stuffing drum, back view (Farrar & Young)

somewhat. They are removed from the drum whilst still warm and are immediately "set out." The advantages of drum-stuffing are not only in speed, but also in the possibility of using harder fats, because of the raised temperature of

the operation. When fats of higher melting point are used, the thinner portions of the leather, *e.g.*, the flanks, are made much firmer, the leather may be caused to "carry" a greater proportion of grease without feeling greasy, and hence much better weights may be obtained. In drum stuffing, such materials as stearin, paraffin wax, wool fat, etc., may be used instead of, or in addition to, tallow and cod oil, but the penetration is often assisted by the admixture of small proportions of degras, sod oil and other materials which lower the surface tension of the mixture to water, and it will be clear to the reader that the correct adjustment of the proportions of these and their temperature of application are matters of considerable importance. It will be also readily understood that if the goods are too wet the greases may not be completely absorbed, and that if somewhat dry the absorption will be greater. Drier leathers are often used in America for drum stuffing than in this country, and hence greater "gains" in weight are obtained, but it has been found on the other hand that if leather is drum stuffed too dry it is very liable to dry out a darker colour, and this is apt sometimes to occur with the flanks which have been insufficiently damped when the goods were put into the drum. A better type of stuffing drum is that heated by hot air instead of steam. It is cooled after the operation by drawing through the drum a current of cold air. Sometimes the drum is heated by means of a steam coil fixed inside it. Drum stuffing is now universal with satin and waxed leathers, etc., and is used in America even for heavier goods.

"**Burning in**" (*Einbrennen*) is a method of stuffing used in Germany for heavy leathers (belting, black harness, etc.) and for goods whose colour is not so important. It involves the use of temperatures of 80—100° C., and this can only be successfully employed with dry leather, for if moisture were present in the leather and raised to this temperature, the fibres would be made tender by its action, and the strength of the leather would be seriously impaired. The great essential of the process, therefore, is to have the leather completely free from moisture, and this is effected by drying in stoves at temperatures not less than 45° C.

The actual application of the greases is made in two ways.

in one of these the hot dry leather is laid flesh side upwards on wooden frames which are supported over a metal-lined trough, and the greases are poured by a ladle on to the flesh side and brushed over the surface to make the distribution even. A second application is usually given to the thicker parts of the leather only. The hides are then put into warm water (50° C.) for about a quarter of an hour, and when soaked are drummed for half an hour. They are then hung up or laid in pile to samm for setting out. This final wetting and drumming is found to be necessary in order to give the requisite pliability to the leather, and probably assists in making more complete the distribution of the fats into the finer interstices as well as the coarser spaces. In this method it is usual to wipe the grain side of the leather with a damp cloth immediately before the application of the greases, in order to prevent any egress on that side of the fats, for otherwise darkening and unevenness of colour would result. In the other method of application, however, the thoroughly dried goods are immersed in the melted stuffing mixture at 80° C. for a few minutes, and when the air bubbles cease to come, the leather is removed, pulled on to a sloping board, wiped on grain and flesh from superfluous grease, and immediately plunged into tepid water for half an hour. They are then placed in warm water (50° C.) until soft, and afterwards drummed, sammed and set out as in the other process. The vessel which holds the melted fats is a steam-jacketed tank, or one heated by gas jets or a steam coil. For both these methods the stuffing mixture is usually composed of stearin, hard tallow, and paraffin wax.

The "spueing" of curried leathers is a phenomenon which may be here considered, as it is largely dependent upon the nature of the stuffing ingredients. It is the name given to exudations from leather in the form of spots, which, when removed by rubbing or other means, always reappear. It may be due to three distinct causes, one being the "striking" of the harder fats as a white exudation (somewhat resembling mould). This may be caused by the unsuitable mixture of a hard fat (*e.g.*, stearin) and a non-drying oil (*e.g.*, neats-foot), from which the harder fats crystallise, or by the formation of

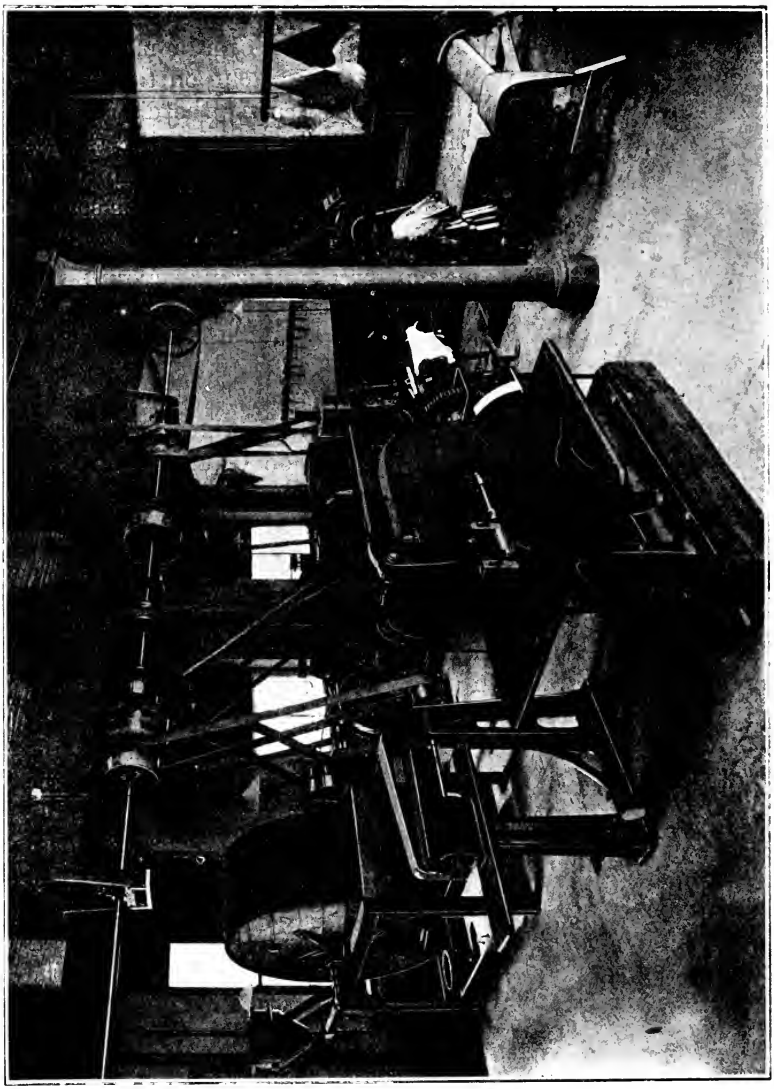


FIG. 86.—Currying shop, Leather Industries Department of the University of Leeds.

free fatty acids from oils which go rancid, this latter being assisted by the growth of moulds whose own development may also cause the mechanical expulsion of the fats. This form of exudation may be removed by petroleum, ether and

benzene, and will melt when held to the fire. A second form of spueing, closely similar in appearance to the above, is due to the presence of inorganic salts (barium chloride, magnesium sulphate, etc.) in the leather, and may occur when the leather is deliberately weighted with these materials, or on boots whose linings are so weighted. Such exudations are unaffected by organic solvents and heat, but may be removed by water. The most annoying form of spueing, however, is due to the oxidation of the oxidisable oils. It appears in the form of pimples of sticky resinous matter, which are the products of the oxidation, and which may in some cases cover the whole surface of the leather. It is clear that it can only be caused by the "drying" and "semi-drying" oils, and that stearin, tallow, sperm oil, vaseline, mineral oil, neats-foot oil and other "non-drying" oils will not yield it. The causes which promote its appearance have not as yet been completely investigated, but those conditions which tend towards the oxidation of oils are clearly undesirable. The presence of free fatty acids, which are more oxidisable than their triglycerides, the presence of oxygen carriers (*e.g.*, iron in the finishing materials), the occurrence of mould or of conditions of moist heat, are all factors which increase the probability of this troublesome appearance. It is a matter of some difficulty to judge from analytical results whether an oil is likely to spue if used in currying, but the iodine value may be considered a measure of possible oxidation, and a high acid value may be taken as an indication of a tendency towards oxidation and rancidity. Oils "rendered" at a low temperature and containing nitrogenous matter have also been shown to be liable to cause this defect. The prevention of the trouble is best ensured by using suitable quantities of non-spueing oils in mixture with the stuffing ingredients, and by the employment of drum-stuffing in which greater proportions of the harder and less oxidisable fats may be used.

The finishing processes for curried leathers are so very variable that no general description is possible, but an outline of the methods in common use for the currying of the more important dressing leathers will now be given.

The currying of strap butts.—On coming from their last

layer liquor these are usually dried out completely, and need first of all therefore to be wet back by soaking in water. This is done by placing a pack in clean, cold water for about twelve hours, the exact time varying with the nature of the tannage. Occasionally the goods are soaked in an old sumach liquor, and sometimes the tumbler is employed. The goods are now laid in pile for several hours at least to soften and make pliable for the subsequent processes. The first of these is the "skiving" on the flesh side by means of the shaving slicker, which is similar in principle to the curriers' knife, but with rounded corners. The pack is now thoroughly scoured to remove the bloom and astringent tan of the surface, and to strike out the leather somewhat. This is still done by hand labour, with stones, brushes, pumice and iron slickers, but machines are being increasingly used. If the Jackson machine is employed, for example, the goods are scoured on the flesh twice, from butt to shoulder, and afterwards from back to belly. The grain side is treated similarly, but receives a third scouring from butt to shoulder. The Burdon machine is often used for scouring the flesh side. After scouring the butts are generally sumached to improve their colour and to restore partly the weight lost in scouring by a slight re-tannage. The goods may be placed in a vat containing a strong infusion of sumach at nearly 100° F. for about a day, handling at least two or three times, or may be drummed in the warm infusion for an hour, or even less. If machine-scoured, the packs are now gone over again with stone and brush, by hand, to remove machine marks and any bloom the machine has missed, and are well slicked out to remove superfluous moisture and thus save time in drying. They are then sammed for stuffing by suspending in a moderately cool shed, and laying in pile for some time to temper, keeping as flat as possible. The stuffing is usually done by hand. The butts are put on the table flesh upwards, and a coating of cod oil is brushed in; the goods are then turned over and evenly stuffed on the grain with a stiff mixture of tallow and cod oil (5 : 4) or some other suitable mixture, using rather less of the grease in the thinner parts. This coating is well brushed, and the goods are hung up again in a temperate heat for

several days to dry somewhat and allow the penetration of the fats. They are then taken down ("rounding for setting"), brushed on the flesh with warm water, and after the moisture has sunk in are given an even coat of a decidedly more liquid dubbin, and carefully piled for several hours at least. The grain is now thoroughly set out by hand, using sharp stones and short strokes. Machines are also used, and the goods are then put through twice, first with a fairly heavy stroke from butt to shoulder and afterwards with a lighter stroke from back to belly. After drying slightly and laying in pile for a few hours to temper, they are often re-set in a similar manner, with lighter strokes, or by hand. The goods are now hung up in a warm shed, partly dried off, and then slicked out and brushed over on grain and flesh to remove superfluous grease, and pebbled or glassed well to remove any marks due to setting, and to make quite smooth. They are now hung up and completely dried out. The process of "rounding" now follows, in which a light coating of tallow is given on grain and flesh, which prevents the grease striking out and assists in giving the goods a nice finish. If they are thought to contain an insufficient quantity of grease, dubbin may be used for the flesh and tallow for the grain. They are now carefully laid away in pile, keeping as flat as possible until they are needed for cutting. They are finished by slicking off the superfluous grease from flesh and grain, and brushing in the rest until glossy. The edges are scraped with a hand-knife.

It is often customary to slit down the back after soaking, especially if not even in substance, and this is also done occasionally after sumaching, but if the goods are level it is often more convenient to dress them whole. This slitting should be very carefully done in a straight line down the part which has been immediately above the backbone. Machines are now available by which this process may be safely and satisfactorily carried out, and these are used also in cutting up the goods into straps.

The currying of harness backs.—There are two principal varieties of harness leather—black and brown—and the currying processes for these naturally differ somewhat.

For black harness the goods may be dried out from the last

layer and treated in the following manner: Soak by dipping into warm water and leaving for some time in pile. They are thus sammed for shaving. In shaving merely the superfluous flesh is removed, and this may be done by hand over the beam, but for the lighter classes of goods by machine, or the goods may be skived with a turned edge slicker. For thick necks the Union splitter is sometimes useful, a previous jacking being given. Scouring follows, and is now almost universally done by machine on flesh and grain, the Jackson and "Climax" machines being popular. This is an important process, and the machine saves much laborious work, but the goods are often gone over by hand afterwards to deal with any patches insufficiently scoured by the machine. The sumaching depends somewhat on the nature of the tannage, but for a good tannage a warm infusion is employed, using about 2 lbs. per hide; the goods are rinsed through, piled for a time, and put in the vat overnight. For some tannages the sumaching lasts several days, with frequent handling and occasionally some scouring; sometimes the goods are drummed in sumach before scouring. The goods are then set out by a slicker, oiled lightly on the grain and hung up to samm till fairly stiff. They are then taken down, damped back in the wet parts, and laid in pile to temper. For first-class goods the backs are now stoned in the "jack" and then "flatted" to remove the marks of the shaving machine. Any weighting with glucose, etc., is also carried out at this stage. Stuffing now follows, and is mostly done by hand, though sometimes with the drum. In the case of drum-stuffing the following mixtures may be used: (1) 30 parts wool fat, 30 parts tallow, 40 parts cod oil; or (2) 30 parts wool fat, 25 parts tallow, 30 parts cod oil, and 15 parts degras. In the case of hand-stuffing the goods are coated with cod oil on the grain, and when this has sunk in somewhat the pack is again gone through, slicking out the flesh and giving a coat of good dubbin, using more in the thicker parts. They are then hung up and dried further, and sometimes then laid away in pile to "mellow." When in suitable condition, they are re-set by slicking off superfluous grease from the grain, brushing with a stiff wet brush, stoning and slicking well,

and heavily glassing. They are then hung up and dried out. Setting machines are used to some extent, and are perhaps especially suitable for drum-stuffed goods, to remove the "grain" worked up by the drum. Goods which are machine-set after drum-stuffing are slowly sammed, stoned in the jack,

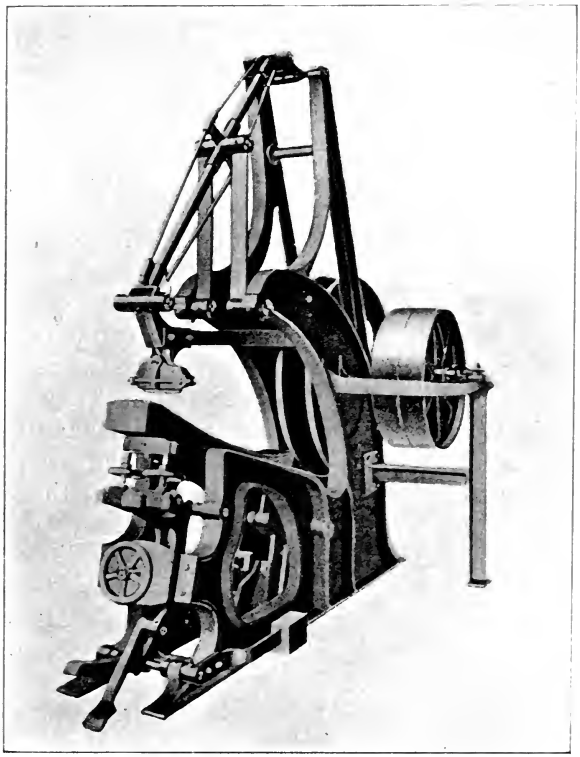


FIG. 87.—Stoning jack (Turner Co.).

re-set by hand and dried out. Buffing is a process now used to a considerable extent at this stage in which the coarser parts of the grain are removed by a buffing slicker or by machine. Goods treated thus are found to be much less liable to crack, especially with the modern economies in the beamhouse and tanyard. Usually, however, this need only be done in the coarser parts. The goods are now blacked

with logwood, ammonia, and curriers' ink, and piled grain to grain overnight. They are then dubbined on the grain with a thin dubbin and laid away for several days, and then set out again by pebbling, slicking and glassing the grain. The goods are then hung up and dried out, buck-tallowed on the grain and again laid away till ready for finishing. The treatment after blacking varies considerably; sometimes, for example, the goods are seasoned, dried and tallowed. In this case a more thorough stuffing and setting must be given before blacking.

In finishing, the backs are cleaned from superfluous grease on both flesh, grain and edges, rubbed and brushed with a stiff brush on the flesh, afterwards glassing well, and slicked and brushed with a soft brush on the grain. Sometimes the flesh is whitened.

For brown harness the process is somewhat similar in general outline, but the goods should be carefully selected with a view to good colour, and afterwards soaked as for black work and shaved (or skived) if necessary. They are then drummed in a sumach liquor for about half-hour at 40° C., and thoroughly scoured. This is an extremely important operation for brown harness, and is best done by the Jackson machine and afterwards going over by hand. They are then again sumached in a fresh, strong and rather hot liquor, handling frequently in a period which varies from several hours up to two days, warming up the vat where necessary. After rinsing from sumach and slicking out lightly on flesh and grain, they are oiled on the grain and hung up to samm. After freeing from sumach, they are sometimes partly sammed by machine, and the drying thereby hastened. Some manufacturers bleach with oxalic acid instead of sumaching, and then samm. After damping back where necessary, they are stoned on the necks, flatted over the beam, set out and hung up to samm for stuffing, which is done by hand. The table is greased with thin dubbin, and the backs set out on the grain with stone and slicker, and then lightly oiled. The flesh is then set out and dubbined rather lightly, and the goods hung up and gently dried in a dark shed. The grain is then well set out with a stiff wet brush and slicker, the

flesh pebbled or glassed, and the goods hung up and dried out at only moderate heat. They are then stained (usually receiving two coats), rolled, lightly dubbined on the grain with thin dubbin, and, after smoothing, hung up again. They are then pebbled well and dried thoroughly. The flesh side then receives a good coat of warm tallow, or a warmed stiff dubbin, which is brushed on with a soft brush, armed off, and the goods are then laid away in pile till wanted for finishing. In finishing, the backs are well glassed on the flesh and rubbed with a soft brush, and on the grain they are brushed, pebbled and rubbed with flannel.

The goods are slit down the back at very varying stages in different shops, sometimes after soaking, and sometimes not until finished.

The currying of waxed kip butts is very extensively carried out in the manufacture of upper leathers, and is typical of the "waxed" leathers, which are all finished on the flesh side. The kips are first rounded, and the butts should be about 50 per cent. of the total weight. The butts are then soaked by damping with tepid water or liquor, and piled for at least one day to samm for shaving. This is now largely done by machine, but for the best classes of goods hand shaving is still preferred by some curriers. The shaving should be clean, or more will have to be taken off in whitening. The goods are then drum sumached in a warm infusion for one to two hours, slicked out, and sammed for stuffing. As with other goods, the sumaching varies considerably with the nature of the tannage. For foreign tanned kips a "re-tanning" is often given in which gambier, oakwood extract, etc., are used in addition to sumach, and the process may then last several days with occasional drumming. The little bloom or dirt in these goods is removed in the sumaching, and hence ordinary scouring is largely dispensed with, but for some tannages it is used, the Burdon machine being employed for the flesh and the Jackson machine for the grain side. Any weighting of the cheaper goods is done at this stage, barium chloride being sometimes added to the sumach liquor. Samming is also frequently brought about by machine or by the hydraulic press, in which latter case the goods may be put straight into

the stuffing drum. For some tannages, however, the press takes out too much tan liquor. Occasionally the goods are completely dried out, and then soaked back and sammed for stuffing. Drum-stuffing is almost universal for these goods, the materials used being hard stearin, wool grease, degras or sod oil, and a little paraffin wax and rosin. Tallow or cod oil are also used sometimes along with these materials. Either of the following mixtures may be used: (1) wool fat, 35 parts; tallow, 25 parts; cod oil, 30 parts; degras, 10 parts; or (2) wool fat, 35 parts; tallow, 20 parts; cod oil, 45 parts. The goods are drummed dry in the heated drum until the temperature is high enough, and the melted grease then run in and the drumming continued for up to two hours, the latticed door then replacing the closed door, and the drumming continued until the goods are cool enough for setting, which is in about another fifteen minutes. They are then slicked on the flesh with a thick slicker or a square-edge glass, and stoned and slicked on the grain, and then dried out in the sheds. The flesh is now lightly "rounded" with dubbin, and the goods "laid away in grease" for three to four weeks to mellow for whitening. In whitening the flesh is first slicked over to remove superfluous grease, and then brushed with a soap solution and the surface whitened with a turned edge slicker. The grain is stoned, slicked out, and "starched" with a solution of a mixture of glue, soap, bichromate of potash, phosphine substitute, and sometimes other materials. They are then hung up to dry for an hour or so and "grained" by boarding the flesh with an arm board, using more pressure on the back and butt.

The "waxing" now follows, and the variation in the composition of the finishes is practically infinite. There are, however, two general types of finish, in one of which the goods are first blacked on the flesh with a mixture of lamp black and oil (*e.g.*, 2 lbs. lamp black and 1 gallon oil), then glassed, hung up to dry, oiled lightly, and "bottom-sized" with a solution of glue (1½ lbs.), soap (1½ lbs.), and logwood extract (2 ozs.) in 1 gallon of water, and, after drying, "top-sized" with an infusion of 2 lbs. glue, 2 pints cod oil, 2 ozs. nigrosine, ½ lb. tallow, 4 ozs. beeswax, 2 ozs. Venice turpentine, ½ gallon water. They are then smoothed over and hung

up to dry. Another type of finish is to use a "soap blacking," which is a solution in water of soap and logwood to which lamp black is added. This blacking can be readily applied by machine work, and the goods are then dried and only sized once with a mixture in which any or all of the materials used for bottom and top sizing may be employed.

The currying of waxed calf is somewhat similar to that of waxed kip. The goods are carefully soaked, often by dipping first into cold water and afterwards into tepid water, piled to equalise, and then made quite soft and flexible by drumming dry for about twenty minutes. They are then shaved clean (usually now by machine), and sumached for nearly an hour at 40° C. For these goods a thorough scouring is now given on both flesh and grain, hand labour being preferred, and the skins are hung up to samm for hand-stuffing, or completely dried out and wet back for drum-stuffing. If the former is employed an ordinary dubbin of tallow and cod oil is used (about 50 per cent. of each), and in drum-stuffing it is often usual to employ a fair proportion of these materials together with some good stearin and degras and a little paraffin wax. After drum-stuffing, the goods are quickly set out by hand, hung up and dried out for whitening; after hand-stuffing, they are hung up until the grease has sunk in, "rounded down" with weak dubbin, laid in pile to mellow, and the superfluous grease slicked off before whitening. The flesh is whitened with the turned edge slicker, the grain coloured by "starching," and the goods are then blacked and finished in a similar manner to waxed kips. E. I. tannages require a more thorough retanning and a greater proportion of the harder greases in drum-stuffing.

The currying of waxed splits is another important section of the waxed leathers, large quantities of this class of goods being dressed for the manufacture of cheap boots. The splits must have a good substance and a fine flesh, and after soaking in tepid water for a short time are run in a tumbler for twenty minutes without liquor. They are shaved as lightly as possible in the light parts and very little in the butt. After drumming in a gambier liquor of fair strength, they are struck out by machine, hung up to samm, damped down in the dry

places and laid in pile to regulate for drum-stuffing. In stuffing, about 40 per cent. of grease is used on the weight of the leather, consisting chiefly of stearin and wool fat. After running until the greases have been absorbed, the goods are cooled somewhat, set out at once and hung up to dry. They are next lightly slicked on the flesh, and whitened either with the slicker or by machine on the split side. The goods are now coloured on the back. A suitable mixture for this is made up from 1½ lbs. Irish moss, 1 lb. glue, ½ oz. ochre, 2½ ozs. nut-brown stain in 3 gallons water. When this is surface dried the goods are glazed by machine and dried out. Waxing now follows. The black is made by stirring gradually 1 bucket of lamp black into a boiling solution of 3 lbs. of soap. After applying this the goods are hung up till ready for pasting. The paste is made by boiling 3 lbs. flour in 3 gallons of water for three hours and then adding to the hot solution 1½ lbs. soap, 3 lbs. tallow, and 2½ ozs. nigrosine. The goods are then hung up to dry, glazed by machine, sized with gum tragacanth to which some nigrosine has been added, dried out and oiled off.

The currying of waxed shoe butts is practically the same as for waxed kip butts, except that after shaving they are well stoned, sammed further, flatted and scoured by hand on the flesh and by machine on the grain.

The currying of army grains is rather similar to that of waxed shoe butts, but the goods are hand-shaved, hand-flatted, drum-sumached, thoroughly scoured by hand, and also hand-stuffed. After whitening, starching and boarding, the flesh is slicked out, French chalked, and thoroughly glassed instead of waxing. Instead of shaving they are now frequently split, first taking off a thin split in the band-knife machine (levelling), and afterwards splitting in the Union machine. The first splits are worked up for linings and the splits from the Union machine curried and finished as for waxed splits.

The currying of satin leather differs from that of the "waxed" leathers in that it is finished on the grain side. This type of dressing is given both to hides and to offal, but perhaps more extensively to the latter (kip shoulders, etc.). The process is, however, practically the same in each case. The

goods are well soaked and piled to equalise for shaving or splitting in the band-knife machine. The latter operation is preferred, but very little is removed as the flesh split is of comparatively small value. The goods are bettter drum-sumached for one hour, and scoured flesh and grain in the Burdon machine, but these operations are now omitted to

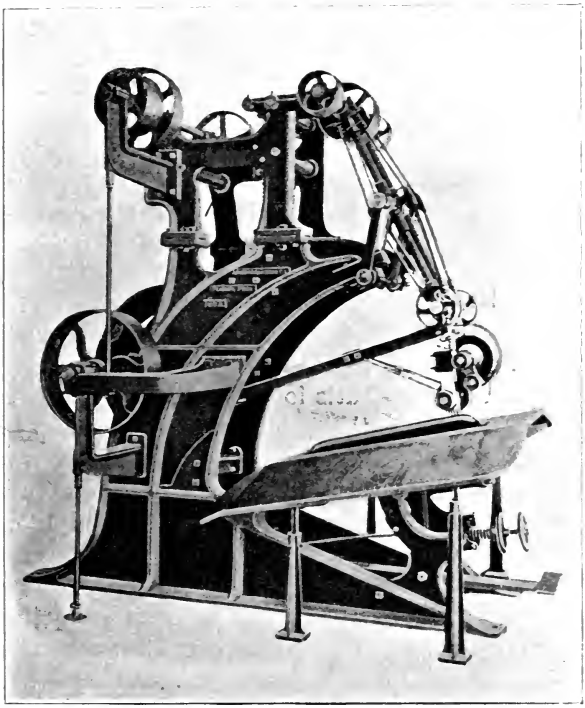


FIG. 88.—Pendulum whitening machine (Turner Co.).

lessen the cost of production. For foreign-tanned goods some re-tannage in gambier, sumach and extract is perhaps necessary. The goods are then sammed for stuffing or dried out and wet back. Drum stuffing is now almost invariably employed, and the goods are afterwards quickly set out, usually now by the Jackson machine, on flesh and grain, and afterwards by hand, but occasionally by hand labour alone.

They are then carefully hung up and dried out. Buffing is the next process, and is important for giving the characteristic silky feel to the leather. The grain is brushed with a hard soap solution, struck out and buffed lightly and evenly with the pendulum whitening machine or turned edge slicker. Blacking follows immediately with logwood infusion (containing a little ammonia) and currier's ink, and after this has sunk in, the black grain is greased with thin dubbin and the goods are horsed up overnight, reset by hand, and hung up to dry. They are then whitened in the pendulum machine (Fig. 88) to clean the flesh, trimmed, bottom-sized and top-sized with careful smoothing, and lightly oiled off. The mode of procedure after blacking varies considerably; for example, it is often usual to bottom-size whilst resetting and afterwards to whiten. The sizes are as a rule specially suitable for this class of finish, but resemble in principle those used for the waxed leathers. **Satin calf** receives a very similar finish, but the goods are often shaved, sumached, scoured and hand-stuffed.

The currying of memel butts for heavy uppers involves also a finish on the grain side, the goods being, however, printed as well as blacked. After soaking back, they are shaved, or a thin split is taken off with the band-knife machine, and then drummed in hot sumach for an hour or so and thoroughly scoured on flesh and grain. The scouring is now often omitted, but, if so, cracky grain is rather apt to occur after printing. When sammed the goods are rather heavily stuffed by drum or by hand. The excess grease is then slicked off and the grain buffed to remove scratches, bad grain, etc., and brushed over with a logwood solution containing a considerable amount of ammonia, and afterwards with currier's ink, after which the butts are hung up till the black has struck and then laid in pile to equalise. The goods are now carefully set out on the grain, somewhat thinly sized, and slowly dried. When surface dry they are printed with a memel embossing roller (p. 340) and then completely dried out. After crippling and graining four ways, they are whitened on the flesh and coated on the grain with linseed oil containing resin; they are then French chalked on the flesh and glassed off.

The dressing of levant, although not involving the stuffing process typical of the curried leathers, is conveniently described here, as it is associated with them, being manufactured from hide and kip offal which have received a dressing leather tannage. The goods are soaked and piled twenty-four hours, and shaved or split to rather light substance, sumached half an hour in the drum, machine scoured, and often weighted, then oiled and hung up to samm. They are now set out flesh and grain, buffed where necessary, embossed on the grain by machine (p. 339), blacked with logwood liquor and currier's ink, dried, boarded, bottom-seasoned (p. 340) with blood, logwood, orchil, and some methylated spirits, dried somewhat, boarded again, top-seasoned, dried again, and glazed (p. 341). They are sometimes grained again, and are sometimes bruised and boarded before blacking instead of between seasoning. They are finally oiled off with mineral oil.

A cheaper method can be carried out in the following manner. The goods (*e.g.*, kip shoulders) are soaked, split to take the thickness off the neck, shaved to required substance, sumached in drum, slicked out, oiled off, and dried. If possible, they are sammed by machine before oiling. They are damped down with logwood on the grain, printed at once, blacked with ink, and dried out. They are softened down with a hand board or machine, bottom-seasoned, fluffed, top-seasoned, dried out, glazed off, boarded up the grain, and oiled off with hot mineral oil. The season is made by dissolving 1 oz. gum arabic in 1 pint logwood liquor, adding 7 pints blood, and afterwards adding a solution of 1 oz. aniline black and 3 ozs. camphor flowers in ¾ pint methylated spirit, and then mixing well. This season should be a few days old before use.

The currying of glove hide bellies may be carried out in the following way. The goods are soaked, sorted, split, and taken straight to the stuffing-drum; a mixture of 3½ parts of paraffin wax and 1 part oil is used for stuffing. The goods are "canked" out on the flesh, set on the grain smartly, and hung up. Another tight resetting is given when sammed. When dried out, they are damped back with soap and water, set out with the slicker, and buffed. The goods are now blacked,

and hung up to dry out. When dry they receive a good size with glue and water, and are then dried out and glazed.

The dressing of lining leather is largely from kip sides. For this purpose large spready kips are chosen, of good colour. They are cut down the back, soaked, split to required substance, and, if not light enough, shaved level, sumached one hour at 45° C., well slicked out, oiled and hung up to samm. The goods are then lightly reset on flesh and grain, with a thin slicker, dried out, trimmed, grained, fluffed on the flesh (p. 343), and the grain dusted with French chalk to give a polish. If the grain is coarse, a resetting may be necessary Damaged grain should be lightly buffed with a slicker. Kip bellies may receive the same dressing, but after soaking and shaving are tumbled in warm water with a little weak oxalic acid. They are then sumached and scoured out with a brass slicker. Sometimes this class of goods is stuffed on the grain side with dubbin and water instead of oiling.

The currying of bag hides. The grains on coming from the last liquor are drummed in sumach paste, rinsed and drained overnight, lightly oiled, sammed over poles, slicked out flesh and grain, and dried out completely. After careful wetting back, they are shaved level, drummed in sumach, scoured by hand, and sumached for two days in somewhat strong liquors. The sumach is then slicked off the flesh, the goods set out, lightly oiled on the grain, sammed, and after tempering back where necessary, reset with slicker on the grain and dried out completely. Staining (p. 329) then follows, and, after samming, printing with the pendulum machine from belly to belly. The goods are now buck-tallowed or dubbined lightly on the grain, and dried. After whitening the flesh the goods are boarded lightly and grained to bring out the print, brushed on the grain and rubbed with flannel.

The currying of bridle leather differs from the dressing of harness backs in that the goods are much freer from grease, stuffing being usually replaced by merely oiling. After rounding rather long butts, they are carefully shaved, sumached, slicked out, dried a little, and oiled lightly but thoroughly with cod oil on flesh and grain. After laying in pile for some time they are thoroughly set out

and dried out completely. They are now scoured on the flesh with brush and warm water, and sized with Irish moss and French chalk. When this has set somewhat, the grain is brushed similarly, re-set by slicking out well, and given two coats of a weak phosphine or other stain, and a coat

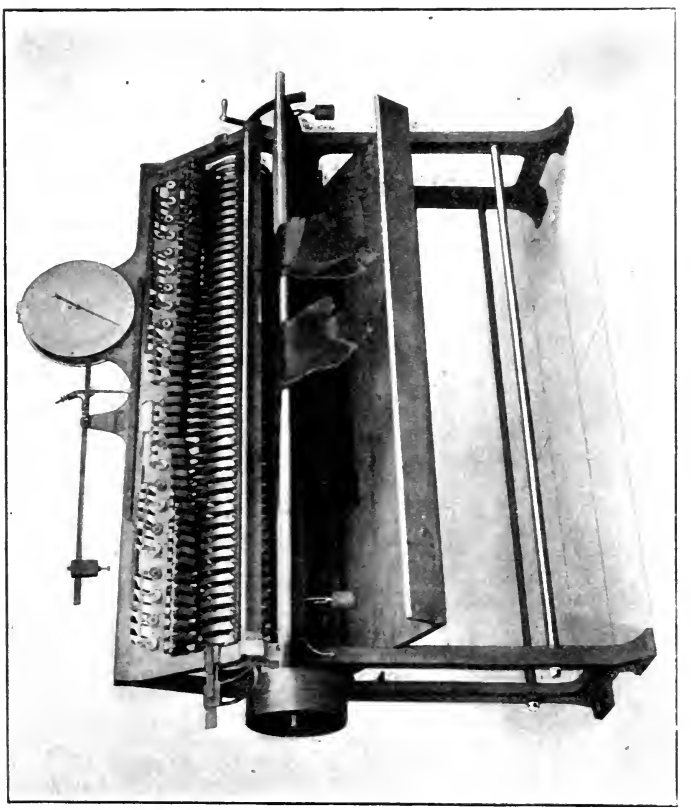


Fig. 89.—Areameter (Farrar & Young).

of gelatin and linseed jelly containing some of the stain. They are then wiped, glassed, and hung up to dry stiff, glassed again heavily on the flesh, and dried out completely. They are then glassed again on the flesh, and the grain rubbed with flannel. Sometimes they are not stained, but, after re-setting, sized lightly with linseed jelly on the grain as well as the flesh, glassed and finished.

The currying of kip bellies for straps may be carried out in any of the following ways :—

(1) The goods are soaked, shaved, sumached, sammed, hand-stuffed on the flesh, and hung up to dry. The grease is then slicked off, the grain cleaned, and the goods seasoned with gum arabic, gum tragacanth, starch and milk, and a little dyestuff.

(2) In this method the dressing is identical with that given above for kip bellies for linings, but at resetting all the stretch must be got out in this case. The goods are also oiled off instead of stuffing as just mentioned. By this method a brighter grain is obtained, but the leather is not so good.

(3) The goods are soaked, shaved, and scoured (using no oxalic acid). They are then fat-liquored with soap and linseed oil, tumbling well for one hour. The bellies are then struck out, hung up to samm, reset tight, dried, and glazed off without seasoning.

The dressing of legging leathers.—The hides for this purpose must be carefully selected and of uniform quality. The grain should be close, and without too much bloom, and it is an advantage to the surface of the flesh side if the goods are split green, or, at any rate, when just struck through with tan. The hides are soaked and the butts shaved perfectly level. They are then scoured flesh and grain in warm water at about 50° C., and sumached for three days, handling at least three times a day. They are slicked out flesh and grain, oiled up with a good coat of linseed oil, and dried out. After dipping through cold water fairly quickly, and stoning on the grain, the goods are flatted. The flesh is now brushed up with cold water, and the grain with warm water, and the goods piled to regulate. The flesh is next given a dressing of Irish moss and tallow, which is evenly spread with a brush, and after setting on the grain and hanging up, the grain is given a very thin coat of gum tragacanth by means of a sponge or soft cloth. The flesh is glassed when half dry, and when quite dry the grain is stained with two coats of the required colour and also glassed. The goods are brushed up by hand or machine, seasoned with milk and water, and glassed by machine.

The currying of picking band butts involves the usual soaking,

shaving, and scouring on flesh and grain. The goods are then preferably sumached for three-quarters of an hour in the drum, slicked out, sammed, and hand- or drum-stuffed with a fairly stiff grease. They are then set out, stoned on the grain, and re-stuffed by brushing on warm cod oil and laying away in pile for several weeks, slicking off and re-oiling at intervals. They are sometimes stained black before stuffing.

Although the heavier dressing leathers are generally sold by weight, an increasing proportion is sold by area, and hence machines have been devised to measure the area of leather with accuracy and speed. The most common type is that shown in Fig. 89.

CHAPTER XXIII

LEATHER DYEING

The art of dyeing leather dates back to prehistoric periods, but until comparatively recently[1] the only colouring matters available were the natural organic dyestuffs, or pigments of mineral origin, and although these are still used in special cases—notably the former for the production of "blacks"—the employment of the artificial organic dyestuffs is now far more extensive, and is slowly replacing the natural dyestuffs altogether. This change from the old fashioned dyestuffs to the more recent "coal tar colours"[2] is doubtless due to the advantages of the latter with regard to their ease of application and evenness of result, which has permitted the shortening and simplification of the dyeing process.

The Artificial Dyestuffs are obtained from the products of the distillation of coal, and may be derivatives of benzene, naphthalene or anthracene, but with their chemical constitution this volume cannot attempt to deal. The majority of them are soluble in water, and most of those suitable for leather dyeing are capable of direct application, *i.e.*, they will combine with leather without a mordant. For practical purposes they are conveniently divided into two classes—basic dyestuffs and acid dyestuffs. The former are salts of organic colour bases (complex ammonias), with hydrochloric acid, but sometimes with sulphuric, acetic, oxalic or nitric acids; the latter are salts of organic colour acids, the inorganic basic radicle being usually sodium.

Basic colours have the property of giving a precipitate with solutions of the vegetable tannins, the acid constituent of the dye remaining in solution and the organic colour base

[1] Prekn's "mauve," the first coal tar colour, was introduced in 1856.

[2] Sometimes called "aniline dyes," from the fact that many of them are derivatives of aniline.

combining with the tannin. Hence the use of tannin in mordanting cotton; the cotton is treated with an infusion of tannin which is partly fixed in the fibres, and afterwards with the basic dye, which is fixed by the tannin. Hence also a 10 per cent. tannin 10 per cent. sodium acetate solution forms a test re-agent for the basic colours, the acetate serving to neutralise any strong acid which might tend to prevent complete precipitation. Another consequence of this property of basic dyestuffs is that they are readily absorbed by the vegetable tanned leathers and therefore need some care in their application. The tendency is to dye too quickly, especially where there is any tannin in excess, and hence it is essential to wash the goods thoroughly to obtain an even distribution of the tannin, and a small quantity of acid (*e.g* acetic) is often used along with the dye to lessen somewhat the rapidity of the dyeing and ensure evenness of deposition. If too much is used, however, there may be difficulties in exhausting the dye-bath, and the dyeing may even be prevented altogether. Acid salts and even neutral salts (*e.g.* sodium bisulphate and sodium sulphate) are found to assist similarly in the production of even colour. It will be clear also that the addition of alkalies would accentuate the difficulty, as other organic colour bases would be precipitated in the dye bath, and this is very liable to occur with waters containing much temporary hardness, giving rise to irregular dyeing and uneven colour, as well as waste of dyestuff. To such waters therefore it is desirable to add acetic acid in making up the dye-bath. Where the basic dyes are not very soluble in water it is also desirable to use some acetic acid in dissolving them. Another point is the possibility of any excess of tannin bleeding into the dye-bath and there causing a precipitation and waste of the basic dyestuff. This loss is liable to be very serious, and has given rise to the process of "fixing," in which the leather is treated before dyeing with a solution of certain metallic salts which react with the tannin and precipitate it in an insoluble form on the leather fibre. Tartar emetic (potassium antimony tartrate) is the most common and useful of these salts, as it gives an insoluble and lightly-coloured tannate, and can be employed in

comparatively small quantities. Antimony lactate, titanium lactate, potassium titanium oxalate, aluminium acetate, and lead acetate are also used. Common salt also assists in rendering the precipitate less soluble. The skins should be thoroughly soaked and washed in order to remove excess of loose tannin and avoid waste of the fixing salt. The fixing may be done in paddle at 30—40° C., or in a tub in which the goods are constantly stirred, and the skins should remain in the liquor at least ten minutes. About 2 ozs. of tartar emetic and 8 ozs. of salt are sufficient for a dozen skivers, and 3 ozs. of tartar emetic and 8 ozs. of salt for a dozen calf skins. After fixing, the goods must be again well washed to remove all soluble salts. Basic colours are also precipitated by acid colours, and therefore mixtures of dyestuffs from both classes cannot be employed.

A great disadvantage of the basic dyestuffs is that they are taken up much less readily by the grain of the leather than by the general substance, so that where there is any weak or defective grain the effect is exaggerated in dyeing.

Another disadvantage of basic colours is their great tendency to "bronze," *i.e.*, to reflect light which is complementary (p. 322) to that transmitted by them and reflected normally from the dyed material. This dichroic effect can be produced by the acid colours as well as the basic colours, but is generally more marked with the latter, especially when somewhat strong solutions are used.

The "Janus dyes" are best regarded as basic colours when leather dyeing, but they possess also the properties of acid colours. The so-called "fat colours" are oleates and stearates of the colour bases. They are soluble in benzene but insoluble in water, and hence can only be used in staining greasy leather and in grease finishes.

Acid colours do not give precipitates with tannin, but are nevertheless capable of dyeing leather, which can absorb acids as well as bases. The full depth of shade is not obtained with these dyestuffs, however, until the colour acid is liberated by the addition of some stronger acid to the dye-bath. Sulphuric acid is generally used for this, a quantity being taken equal to the weight of the dye, but its use is liable to cause eventually

the decay of the leather, so that where permanency is important formic acid should be substituted for it. Sodium bisulphate is also used in place of sulphuric acid, and gives a distinctly slower dyeing, and consequently a more even result, whilst at the same time the risk of damage to the leather is said to be far less than with the free acid. The risk of injurious effect can also be much decreased by using very weak dye liquors, and the concentration of the sulphuric acid in the bath should never exceed $\frac{1}{4}$ per cent. Some of the acid dyestuffs dye well without the addition of acid. After dyeing with acid colours and an acid, the goods must be well washed to remove all excess of free acid, and where sulphuric acid has been used the addition of salts of weak acids to the water used for washing is desirable to minimise the risk of decay. Sodium or potassium acetate, lactate, tartrate or citrate may be used for this purpose, but the excess must be carefully washed out.

The acid colours are usually preferred for leather dyeing because they do not dye more deeply where the grain is defective as the basic colours do, and, moreover, they are as a rule much less fugitive to light and much more free from the tendency to bronze. They have not, however, such a great colouring power as the basic colours, and hence it is sometimes a good plan to "bottom" with an acid colour and "top" with a basic colour.

The so-called "direct cotton dyes,"[1] which dye cotton without a mordant, belong to the class of acid colours, and many of them are suitable for leather dyeing. When used in neutral or slightly acid baths they give even and pale "art" shades, but when fully acidified give full, deep shades. The addition of common salt or sodium sulphate to the dye liquor hastens the dyeing with these colours by decreasing their solubility, and it also assists in the exhaustion of the dye-bath, but gives rise to the necessity for thorough washing after dyeing.

The "eosines" are also acid colours, but are precipitated by mineral acids and by many basic and acid dyestuffs. Hence they are best used without admixture with other dyes and in

[1] Including the "Congo," "Mikado," "sulphamine," "benzidine," and "sulphide" colours.

conjunction with acetic or formic acid. They produce fine pink shades, but are very fugitive to light.

The "sulphide colours" have to be dissolved in a weak solution of sodium sulphide, and hence are difficult to apply to leather without damaging the grain. They form fast colour lakes on chrome leather, however, and permit the use of alkaline fat liquors.

The "mordant dyes" are acid dyes which require a mordant in dyeing. They include the alizarine dyestuffs.

Commercial dyestuffs very often contain dextrin, common salt, sodium sulphate and other substances as impurities. These are partly used to permit different batches of the same dyestuff, being adjusted to the same colouring power, and to dilute dyes of extremely great colouring power, but also to a very large extent merely to adulterate and permit sale at a lower price. Many commercial coal tar colours, *e.g.*, many "browns" and "blacks," are also mixtures of two or more distinct dyes. If these have been mechanically mixed in the dry state the admixture may often be detected by distributing a very small amount of the dyestuff over wet blotting-paper, each particle of dye then producing a spot of its own colour. The same test can be applied by distributing over alcohol and over sulphuric acid, and often gives additional information.

The colouring powers and relative strengths of commercial dyestuffs may be compared best by actual dyeing tests with small pieces of sumach skiver. The pieces may be about 8 inches by 4 inches, but should be equal in area, and the dyes should be taken in equal quantity and dissolved in the same amount of water. The dyeing may be done in photographic dishes or by suspension in glass vessels inserted in a water-bath. To compare the relative cheapness of dyes, the quantities taken should not be of equal weight but of equal monetary value. That which gives the deepest shade of colour is then the cheapest dye.

In dissolving the coal tar colours the best method is to pour hot water on to the dyestuff in a wooden vessel, stirring constantly and adding sufficient water to dissolve all the dye. With acid colours boiling water should be used, but with basic colours the temperature should not exceed 85° C., as many of

these colours are decomposed at higher temperatures. When a perfectly clear solution cannot be obtained, the infusion must be filtered through canvas, as otherwise there would be a liability to spots and streaks, especially if the infusion is to be used for staining. Difficultly soluble colours may be mixed to a paste with a 10 per cent. acetic or formic acid solution, and hot water then used as usual. Methylated spirits or glycerin can also be used to assist the solution. Acid dyes require usually from fifteen to twenty times their own weight of boiling water, but basic dyes are distinctly more insoluble and require from twenty to forty times their own weight of hot water. The concentration of the dye in the dye-bath varies considerably according to the colouring power of the dye and the precise shade required, but may be between $\frac{1}{2}$ and $2\frac{1}{2}$ gms. per litre.

The Natural Dyestuffs still find a place in leather dyeing and staining, but by far the most common of those now used is **logwood.** This is obtained chiefly from British Honduras and Jamaica. It is chipped up and exposed to the air in a slightly damp condition ("ageing") until the hæmatoxylin it contains is oxidised to hæmatin, and the colour of the wood changes from a light yellow-brown to a full red-brown. An infusion is made by means of boiling water, but several extractions must be made for complete exhaustion. No alkali should be added during extraction, as this causes a loss of colouring matter due to oxidation and precipitation. Logwood extracts[1] are now on the market in both solid and liquid form, and, being more convenient to the leather dresser than the wood, they are being largely adopted. The cheaper extracts are often considerably adulterated with glucose, dextrin, salt, sodium sulphate, tanning extracts, etc. Logwood is most widely used in producing blacks with iron salts. In staining vegetable tanned leathers a somewhat strong infusion is used which has been made slightly alkaline with ammonia or sodium carbonate. This is brushed on to the leather. The function of the alkali is to assist in wetting greasy leather, and also to combine with the acid of the iron salt or "striker" and thereby assist in the formation of a colour lake. Excess

[1] Including "Hæmatein," "Hematine," "Hemol," and "Hemolin."

of alkali should be avoided, or the quality of the leather will be affected. The iron mordant is brushed on to the leather after the logwood infusion and may consist of ferrous sulphate, iron nitrate, or of iron liquor. A little potassium dichromate is often added, which oxidises the hæmatoxylin to hæmatin and the ferrous salts to ferric salts, and the chrome salt formed also gives a black logwood lake. A little copper sulphate or acetate is also often used to give a deeper black and one which is less fugitive to light, and brazilwood extract may also be added to the logwood infusion for the same purpose. Fustic, sumach, quercitron bark, and galls are used in small quantities along with logwood to assist in giving a dead black, for logwood alone gives blue- or violet- blacks. The logwood solution may suitably contain 3 per cent. logwood extract, $\frac{1}{4}$ per cent. fustic extract and $\frac{1}{8}$ per cent. soda crystals. The "striker" may suitably be a 3 per cent. ferrous sulphate $\frac{1}{2}$ per cent. copper sulphate solution. Excess of iron should be avoided just as much as excess of alkali, especially when there is no excess of tannin, for it will make the leather brittle and is apt to cause spueing in curried leathers. It is therefore often a good plan to brush over the goods a second time with the logwood infusion after the iron solution has been applied. This is particularly true when the commercial "inks" are used, for these nearly always consist of ferrous sulphate to which a small amount of tannin or logwood has been added, and therefore contain excess of iron salt. They often contain also aniline blacks and starchy materials. Coal tar blacks are generally dark violets to which yellows and browns have been added. Their use is, however, slowly replacing the use of logwood and iron. Logwood is also used for dyeing blacks on chrome leather. In this case a much weaker infusion is employed as a dye-bath, and fairly high temperatures, up to 80° C., may be used. In weak acid solution, and along with various artificial yellow dyestuffs, logwood may be used as a stain or "bottom" for giving yellow-browns for bag work, etc.

Fustic[1] may be obtained in chips of the wood, of which the best qualities come from Cuba, or as a solid or pasty extract.

[1] Called also "Cubawood" and "yellowwood," and obtained from *morus tintoria* which grows in Central America.

It gives a greenish leather with chrome mordants, and is used along with gambier as a "bottom" in dyeing browns on chrome leather.

Brazilwood and the other "redwoods"[1] contain colouring matters of the brazilein class which give red shades with alum mordants and reddish-violet with chrome. They are used to some extent in bottoming when dyeing reds on skivers and mineral tannages.

Cochineal, a dried Central American insect, contains a colouring matter (carminic acid), which with tin mordants (stannous chloride) produces brilliant scarlets which are very fast to light. It dyes even more brilliant scarlets when a little fustic or other yellow colour is used along with it.

Orchil liquor is obtained by the oxidation of an infusion of certain lichens in the presence of ammonia. **Cudbear** is the powdered residue of the evaporated liquor. This colouring matter requires no mordant, and is still considerably used in neutral solution for dyeing maroons for upholstery and for topping maroons in finishing. Its advantage is that it is fairly fast to rubbing.

Cutch (p. 138) in 2 to 3 per cent. solution dyes vegetable tanned leather pale brown without the use of any mordant, and is used for a ground colour in dyeing browns. A 10 per cent. infusion, to which 5 per cent. of soda crystals has been added, is also used for staining deep dead blacks. These blacks are much faster to light than those from logwood and iron.

Indigo is used to a very small extent for dyeing blues on bookbinding leathers. An infusion is made in a vat to which ferrous sulphate and slaked lime are added, and the goods are inserted for several hours, rinsed through weak acids, and hung up to allow the development of the colour by oxidation.

Mordants are chemical substances used to assist the fixation of the dyestuff on the fibres of the material under treatment. The use of iron salts as mordants for logwood has already been mentioned. Ferrous sulphate[2] ($FeSO_4$, 7 H_2O) is very widely used for this purpose, and is cheap, but "iron liquor,"

[1] Including "Peachwood," "Limawood," "Sapanwood," and "Pernambucowood."

[2] Copperas, or green vitriol.

obtained by dissolving scrap iron in crude acetic (pyroligneus) acid, which yields an impure ferrous acetate, is really to be preferred, as its acid has a less injurious effect on leather; but it is rather liable to communicate an objectionable tarry smell to the leather. "Nitrate of iron" consists of a solution of ferric sulphate, ferric sulphate nitrate, and basic ferric sulphate nitrate. It is made by the action of a mixture of nitric and sulphuric acids on ferrous sulphate, and is found to give deeper and bluer blacks when used with logwood on chrome leather. The use of aluminium sulphate, tin chloride, copper sulphate[1] and acetate as mordants has also been noted above. Basic chrome sulphate is used for mordanting oil-tanned leathers. Vegetable-tanned leather is of course already mordanted with tannin, chrome-tanned leathers with chrome salts, and alum-tanned leathers with alumina salts, but the mineral tannages are often mordanted with the vegetable tannins, *e.g.*, gambier. The fixing agents for tannin mentioned in connection with the use of basic coal tar colours are also often termed mordants. Where the colouring matter can be absorbed by the fibre alone the mordant may be added afterwards to modify or develop the colour. This is called "saddening," as the colour is usually darkened, as with logwood and iron salts.

Bleaching is often desirable where very pale or very brilliant shades of colour are required, and with the oil tannages there are quite a variety of methods that may be employed (see p. 377) to give a white colour, but with the vegetable tannages the only method available for giving anything near a white colour is the so-called "lead bleach," which is merely a process of pigment dyeing. The skins are sumached, lightly rinsed and paddled or drummed for an hour in a solution of lead acetate of $\frac{1}{2}$ to 1 per cent. strength. They are then run in a sulphuric acid bath of $\frac{1}{2}$ per cent. strength, which causes the precipitation of white lead sulphate on the surface of the leather, and when white they are removed and "sweetened" by washing in several changes of clean water. The bleaching may be repeated if the requisite degree of whiteness has not been obtained. It will be noticed that this "bleach" does not

[1] Bluestone, or blue vitriol.

remove any colour, but merely covers it up. Dyed leathers may be bleached to a considerable extent, or "stripped" by drumming or paddling the goods in solutions of weak alkalies, such as borax, soft soap, weak sodium carbonate, and afterwards in dilute solutions of weak acids, and then sumaching a 45° C. The use of acids and of zinc and sodium hydrosulphites has also proved very effective in some cases.

Colour Shades are obtained by mixing the various commercial dyestuffs in the dye-bath, but it requires an intelligent comprehension of the principles of colour mixing before satisfactory work can be done.

A beam of sunlight is composed of a great number of different coloured rays of light which, when dispersed by a prism or other means, form a *spectrum*, and which may be re-combined by mirrors or lenses to produce a beam quite the same as the original. If this beam of light fall on an object, certain rays are absorbed and the rest reflected to the eye, where they produce a monochromatic sensation which we term the colour of the object. An object is white therefore because it reflects all the rays of the beam; another object is green because it only reflects the green rays; and another object is black because it reflects no light at all. Colour, therefore, is due to the elimination from white light of some of the rays which constitute it, and is therefore always darker than white light. It is now known that the three primary "colour sensations" are red, blue-green and violet; that by mixture of *light* of these colours all other colours, including white, can be produced. In pigments or dyes, however, we are not dealing with substances whose colour is monochromatic, but with bodies which reflect other rays besides those which are predominant, and in practice the pigments which appear red, yellow and blue, may be considered the primary "colours," and by mixing these in suitable proportions any other colour or shade may be produced. It must be borne in mind, that in mixing these pigments we are not adding two different coloured rays of light, but are making the sum of two different subtractions from white light, and the result is therefore a step towards black, and is indeed always darker than either pigment alone. Thus a "yellow" dye absorbs

violet light and reflects red and green light, which combine to give the colour yellow; a "blue" dye absorbs red light and reflects green and violet light, which yield the colour blue. A mixture of these yellow and blue pigments absorbs both violet light and red light, and reflects only green light, and the mixture therefore appears a green colour; but this colour is a darker green than would be generally obtained from green dye consisting only of one substance. Furthermore, if a red dye be mixed in with the yellow and blue dyes green light is absorbed also, and hence the mixture appears darker, and if sufficient be added no light at all is reflected and the mixture appears black. It is clear also that if red and green dyes are mixed the effect is just the same, and black is produced. The colours of two such dyes or pigments are termed *complementary*, for one absorbs all the rays which would be reflected by the other. In a precisely similar manner a red dye and a blue dye absorb green light and red light respectively, so that in mixture only violet is reflected. Hence also violet is complementary to yellow, and when mixed with it produces black. Whether the result is a dead black or not depends upon the precise shade of the reds, yellows and blues employed as primaries, and upon the proportions in which they are mixed; and although it is theoretically possible to produce any shade whatever by approximate mixture of these colours, in practice this is only very nearly true, for pure primaries can never be obtained.

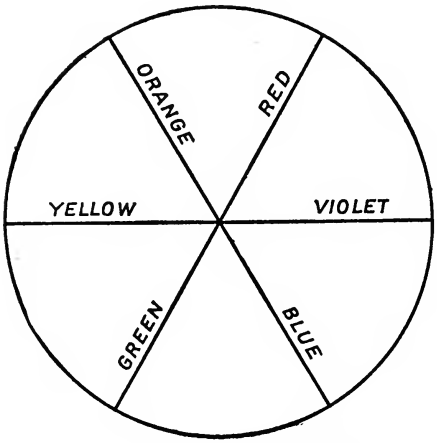


FIG. 90.—The chromatic circle.

The chromatic circle (Fig. 90) is a convenient way of finding complementary colours, such colours being always at opposite

ends of one of the diameters of the circle. The following table, given by Lamb, shows also complementary colours and some acid dyestuffs which may be taken to indicate the shade:—

PAIRS OF COMPLEMENTARIES.

Red . . .	Fast Red.
Bluish Green .	Fast Green Blue Shade, or Cyanole
Orange . .	Orange II. or Mandarine G.
Dark Blue . .	Bavarian Blue or Lanacyl Blue
Yellowish Orange	Orange G., or Crocein Orange G.G.
Reddish Blue .	Acid Violet 4 B., 6 B.
Greenish Yellow .	Quinoline Yellow.
Violet . . .	Acid Violet R.
Yellowish Green .	Acid Green G.G.
Crimson . .	Fast Scarlet B.
Green . . .	Acid Green B.B.
Reddish Violet .	Acid Violet 4 R. or Bordeaux.

When two primary colours are mixed, *secondary* colours are obtained, *e.g.*, green from yellow and blue, violet from red and blue, orange from red and yellow, scarlet from yellowish red and pure yellow, and it is clear that if brilliant shades are to be obtained only two primaries should be used. When any quantity of the third primary is introduced a certain amount of black is practically added. The resulting colour is darker and duller, and *tertiary* colours are produced. Thus if blue (or black) is added to bright orange a brown is produced; if green is added a yellow-brown is formed; if violet is added a red-brown is obtained. Similarly if red (or black) is added to green a dark green results; if a yellow-green is started with an olive-green is obtained; if a blue-green is used a sage-green is produced. These tertiary colours can of course be produced in a great variety of ways, for there is no need to use always a primary colour for mixing with the secondary colour. Thus although maroon can be produced by adding yellow (or black) to purple, it can also be produced by adding greenish blue to orange-red.

It will be clear, therefore, that an enormous number of shades may be obtained from a comparatively few fundamental

colours, and that if the dyer has a thorough grasp of the principles of colour-mixing and takes advantage of the fact that complementary colours produce in mixture a proportion of black, he may effect a very considerable economy of dye-stuff by selecting those colours which are cheapest. Dyeing to pattern is also a matter which requires a clear understanding of the principles of colour-mixing. If the pattern has a dull finish it is best to "wet it back" for comparison with the pack which is being dyed, but if glazed the dry pattern is best for comparison. Allowance must be made for any alteration in shade which may be produced by the materials used in finishing. Where artificial light must be used dyeing to shade is often a difficult matter, for most artificial lights are deficient in blue and violet rays, and objects appear therefore redder and yellower than is actually the case. Goods dyed to shade in artificial light may appear quite different from what is required when afterwards examined in full daylight, and this is especially the case where a fair proportion of blue is involved, as in dyeing drabs, slates, greys, olives, etc. When some amount of dyeing must be done by the aid of artificial light it is much the best to choose the oranges, reds, yellow-browns, bright greens, etc., and to reserve the blues, dark greens, dark browns, violets, etc., for daylight. The electric arc light is the best artificial light for this purpose, and for occasional examination burning magnesium ribbon is a good source of light. The acetylene light is to be preferred to gas or electric incandescent lights.

Methods of Dyeing.—There are four distinct methods of dyeing leather, which involve the use of tray, paddle, drum and brush respectively.

The tray method consists in immersing and working the goods by hand in a shallow box or tray containing the dye infusion. The skins are "paired," *i.e.*, they are sorted into pairs of nearly the same size and shape, placed flesh to flesh and slicked on both grains to make them stick together, and sometimes left in pile for a time.[1] They are thus dyed in pairs and on the grain side only, which condition is required

[1] Large skins are often "pleated," *i.e.*, folded down the centre of the back.

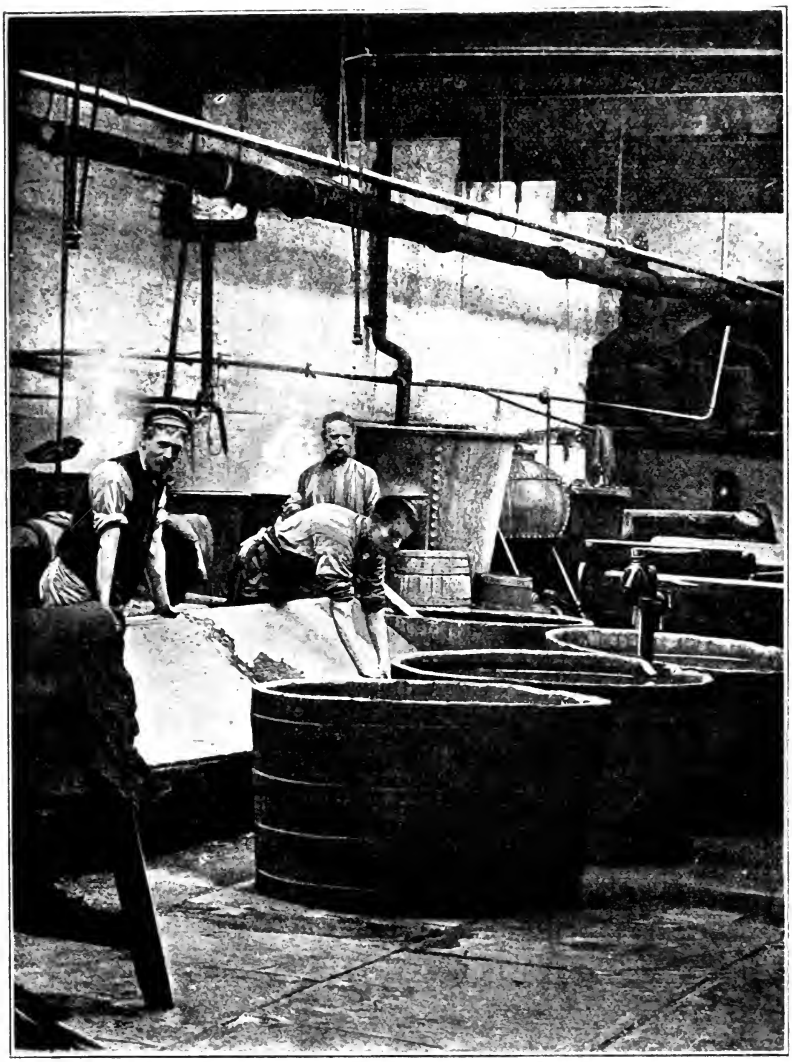


FIG. 91.—Striking out after dyeing (Messrs. E. & J. Richardson, Newcastle).

for some leathers, and at any rate effects considerable economy in dyestuff. There are several ways of operating in this method of dyeing. In the "dip" method, one pair of skins

is dyed at a time, being repeatedly drawn through the liquor by the shanks until the required depth of shade has been reached, which takes usually about five minutes. The disadvantage of this mode of manipulation is that concentrated solutions of dye must be used in order to maintain a reasonable speed in dyeing, and that consequently no exhaustion of the dye-bath is possible and much dyestuff is wasted. In the "one tray" method a pack of skins are all placed in the dyeing tray after pairing, and handled in the liquor until the process is complete. If the pack consists only of a few skins, say about one dozen, a convenient way of handling is to lift up the pair at the top, turn them over, and place them at the other end of the tray; the next pair is similarly lifted, "turned," and placed on the top of the first pair, and the rest are treated in the same way. The process is now gone through again, placing the skins at the other end of the tray, and this should be repeated ten to twelve times until the goods are dyed. If a large pack were treated in this way one skin would remain too long at the bottom of the tray, and it would be difficult to ensure evenness of action. If the skins are small in size a convenient way is continually to pull out the bottom pair, "turn" them, and place them at the top of the pile, until each pair has been at the bottom ten to twelve times. If the skins are somewhat heavy they may be conveniently handled by combining the above two ways. The top pair is lifted, turned, and placed at the other end, and about one-quarter of the pack is gone through in this way. The pressure is now relieved and the bottom pair may be pulled out, turned and placed on the top of the pile at the other end, and this is continued until they are all turned. The process is now repeated until the goods are sufficiently dyed. Whichever method of handling is employed the liquor is strengthened during the process with dye infusion. In the "two-tray" method, which is often used on the Continent, the goods are divided into pairs, and each pack passes through three baths of dye liquor—a weak liquor about 30° C., a moderately strong liquor at about 40° C., and a liquor of the full strength desired at about 50° C. The green pack is placed in the weak liquor in one tray and, after some handling, is transferred to

the "medium" liquor in the second tray, where it is also handled The old weak liquor is now exhausted and run away, and a strong, hot liquor is poured into the first tray. The goods are now transferred to this liquor, and the old medium liquor in the second tray becomes the weak liquor in which the next pack is placed. When the first pack has been handled sufficiently, it is removed, and the liquor left is used as the medium liquor for the second pack, the strong liquor for this pack being then made up in place of the used weak liquor in the second tray. Hence each liquor receives three packs of goods and becomes in turn the strong, medium and weak liquor of the set. There are several advantages of the two-tray system—a much better exhaustion of the dye-bath is obtained, and hence economy is attained; the last liquor may also be fairly concentrated, and a full, even shade may be thereby ensured; the process is quicker than those previously mentioned, and permits an easy calculation of the quantity of dyestuff to be taken for any amount of goods.

The advantages of all tray methods are the facilities for observation when dyeing to pattern, and the economy and convenience of the clean undyed flesh side. The disadvantages are that much labour is required to keep the skins constantly in motion, and that the baths which should be at 45—50° C. soon grow cold and slow-acting unless constantly heated in some way. Where mixed dyes are used, the gradual exhaustion of the liquor by several packs may be at different rates for different dyes on account of their varying affinity for the fibre, and hence a different shade may result. For tray methods, therefore, it is much the best to use single dyes.

The paddle method of dyeing consists in inserting the goods into warm water in a paddle and gradually adding during motion a solution of the dyestuff. The water should be at 55—60° C., and will be cooled down to 45—50° C. by the immersion of the cold skins. Care should be exercised in the addition of the dye solution, or one or two skins will receive a local excess of dye and become stained. The bye solution may be conveniently added to the paddle liquor in four portions at fifteen minutes intervals. The paddle box

should be semi-cylindrical in shape in order to ensure continual motion of the goods and therefore even dyeing. The liquor is apt to cool somewhat, but not so much as with the tray method because of the larger volume. The rate of cooling may be much decreased by the use of a hood or lid to the paddle, and a steam pipe at the bottom of the paddle is also sometimes employed. The advantages of this method of dyeing are that very little labour is required, a large pack can be evenly dyed at one time without difficulty, and the goods are continually under observation except when the lid is down. The great disadvantage of the method is the waste of dyestuff which it involves, for not only is the flesh side of the goods dyed, but the dye-bath is never exhausted and is of considerable volume.

The drum method of dyeing is in many respects the best The goods are first run in a little water, or even without water, and the dye solution is gradually added through the hollow axle. The drum should be fitted with shelves rather than pegs, and as it revolves the goods are continually being immersed and removed from the dye liquor. The advantages of this method of procedure over the paddle method are evident. A much smaller volume of liquor may be used, better exhaustion of the dye-bath is attained, and a considerable economy of dyestuff is consequently effected. The tumbling of the goods gives better penetration and level shades, and the closed wooden drum allows very little heat to escape. On the other hand the method has the disadvantages that the flesh side is dyed and that the goods are not under observation. This last inconvenience can be minimised by using drums with doors that can be easily removed whilst the drum is in motion. With the ordinary cylindrical drum it is obvious that the door should not be in the staves or in the "head" near the circumference, for in these cases the door would have to be heavy and water-tight, and could not be removed during the operation. The insertion and removal of the goods is, moreover, rather inconvenient. If, however, the door is in the centre of the head, a very light and readily removable door may be used with little danger of leakage even when the door is removed, and the arrangement affords

full facilities for the insertion, inspection, and removal of the goods. Other shapes of drum may, of course, be used, and where the goods need some knocking about the polygonal, cubical, and eccentric drums may be appropriately employed. Facilities for running off the liquor in any position of the drum and during motion, and thermometers for ascertaining the internal temperature are also to be desired. A steam-

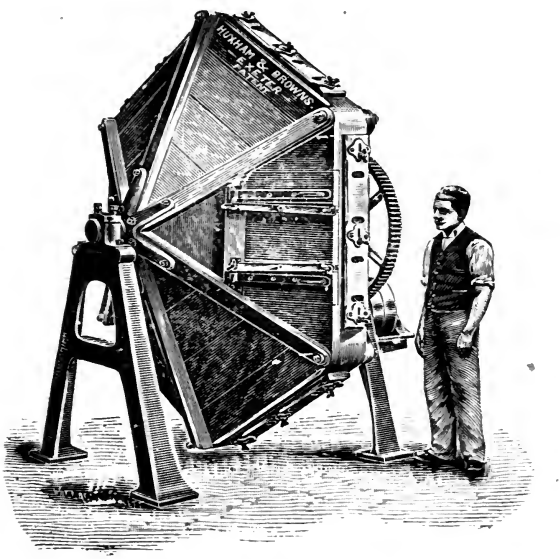


Fig. 92.—Polygonal tumbler.

jacketed pan for dissolving the dye and keeping warm the solution are also often attached.

Brush dyeing or staining is found useful when hides and other goods of large weight and area are being coloured, and also when the flesh side is to be kept clean. It is also useful for alum-kid, in which case immersion in a dye liquor would involve considerable loss in alum. Comparatively strong solutions ($\frac{1}{4}$ to 1 per cent.) of dye are used in this operation, and the liquor is rapidly and evenly brushed over the grain surface with a soft-haired brush. In staining the smaller goods, *e.g.*, basils, the skins may be laid in pile grain upwards and brushed over and hung up to dry in turn. With goods of

considerable area, such as hides or kips, two and sometimes three workmen may operate on the same hide, working from opposite corners and brushing on the same liquor to the same extent. Considerable care must be exercised in joining up the stained parts, or markings will occur. The goods should be in a damp condition, and if somewhat dry they should be brushed over with water or a very weak stain solution before using the strong liquor. After applying the strong stain the goods are hung up to dry and a second coat then applied. A third stain may be given also if the full depth of shade has not been attained. The acid colours are most suitable for this class of work on account of their freedom from bronzing and from exaggerating weak grain, and such colours should be chosen as will readily "bite" in the cold and without the addition of acid, or at any rate with only a weak acid, such as acetic acid. Mucilages of linseed jelly, gelatin, Iceland and Irish moss, starch, etc., are often applied as "sizes" to prevent too deep penetration of the stain and to fill up defective places. Unless the goods have been oiled with a mineral oil after setting, the addition of a little methylated spirit to the stain is desirable. Machines have been devised for brush dyeing in which the dye liquor is fed on to a cylindrical brush under which the goods are made to pass.

The theory of dyeing need not be entered into very deeply. The absorption of the dye by the fibre has been considered a case of chemical action, of physical action, and even as a case of "solid solution," but it is highly probable that more than one type of action comes into play and that possibly all these theories may be true to a certain extent. It would appear, however, that with vegetable tannages the determining factor is the formation of colour lakes with the tannin on the fibre. The tannins are of an acid nature and fix the basic dyes with great readiness, but the basic chrome tanned leathers fix the basic dyes much less readily than the acid dyes, so that it is clear that the nature of the tannage has considerable influence in the matter. In view of these facts it might also be well to consider whether the amphoteric nature of the gelatinous hide fibre is not also an important factor. A practical consequence of this is that chrome leather should be mordanted with

vegetable tannin, or by means of a slight vegetable tannage, if basic dyes are to be used. That chemical action does come into play in some measure is further indicated by the difference in absorbency of the hyaline layer from the substance of the skin, the grain being less absorbent for the basic colours, and more absorbent for other colouring matters, such as the phlobaphenes, which are of an acid nature.

CHAPTER XXIV

THE FINISHING OF LIGHT LEATHERS

Many of the mechanical operations which are used in the finishing of light leathers are identical with those used for the curried leathers, *e.g.*, soaking, shaving, splitting, sumaching, scouring, striking out, setting, etc., and no further description of these processes is therefore necessary.

In preparing skins for dyeing, the nature of the tannage must be taken into consideration. Goods of different tannages often take dye very differently, and complications may, therefore, arise if skins of two different tannages are in the same dye-bath. The catechol-tanned leathers dye much more readily than the pyrogallol-tanned leathers, with the striking exception of the sumach tannages, which dye excellently. With mixed tannages bloom should be removed as far as possible, and dark coloured tannages should be "stripped" by tumbling the goods in $\frac{1}{4}$ per cent. solution of a weak alkali at 30—35° C. For this purpose $1\frac{1}{2}$ to 2 ozs. of soda crystals, 2 to 3 ozs. of soft soap, 2 ozs. of borax or $\frac{1}{2}$ oz. (liq.) of ammonia should be taken for each dozen skins. With East India sheep and goat skins ("Persians") the alkali assists in the removal of the oil as well as a great part of the tannage. Skins treated thus with weak alkalies are washed well to remove the excess of alkali, especially where soaps have been used (or formed from the oil), and are inserted into a "sour" of weak sulphuric acid (a $\frac{1}{2}$ per cent. solution). The skins, darkened somewhat by the treatment with alkalies, are now brightened considerably and prepared for receiving bright shades of colour, but this sulphuric acid treatment has a very detrimental effect on the quality of the leather, and hence it is important to remove as much as possible by thorough washing. Such goods are generally sumached after souring or "clearing" to re-tan and bleach further and to fit the goods for dyeing. It is also

advisable to sumach goods which have been kept for some time in the crust state. The light-coloured tannages should be

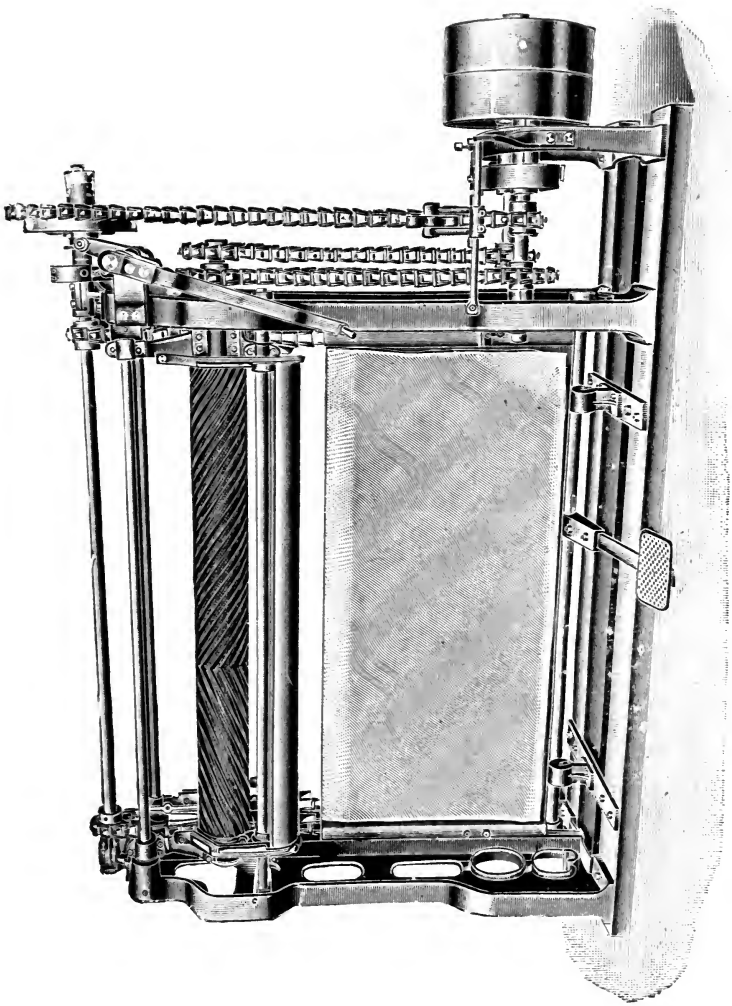


FIG. 93.—Single table putting out and striking out machine (Turner Co.).

sorted out from the crust skins and reserved for bright-coloured dyes.

The machines used for striking out light leathers differ

somewhat in type from those used for the curried leathers. In the most common form (Figs. 93 and 94) the skins are placed over a vertical table which passes between two spiral knife-blade cylinders that work on the skin by revolving in the direction opposite to that of the motion of the table. The table returns to its original position by its own weight, and the pressure of the spiral slicker on the skins is adjusted by a foot lever. It will be understood that the ridge of the skin at the edge of the table is not set out and that consequently the skin must be shifted in position and put through the machine again. Many modifications of this machine are on the market. In one form

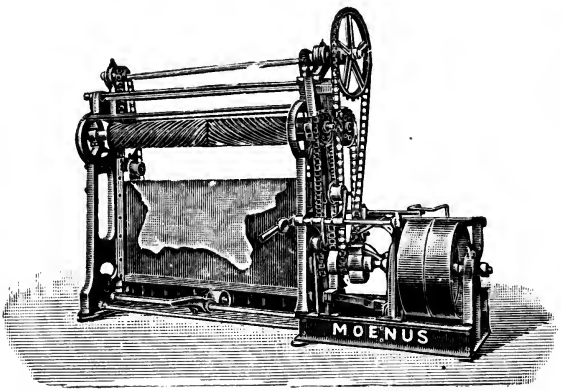


FIG. 94.—The "Tabula" setting out and scouring machine.

(Fig. 95) there are three or more vertical tables and two sets of spiral rollers and these are arranged to work serially and continuously, and to shift the position of the skin automatically, after setting out the first time (cp. Fig. 26, p. 72). Goods are struck by these machines before drying out to the crust, after wetting down from the crust, and usually both before and after dyeing.

After dyeing, the skins are dried out either by hanging up by the hind shanks or by "straining," in which latter method they are nailed out on boards. The former method gives a plump and mellow leather with a soft feel, but very light and thin skins (*e.g.*, skivers) are apt to take up an irregular stretch and are, therefore, better strained. Straining is also to be desired where the maximum area is to be obtained, or where

setting is omitted with cheap goods (*e.g.*, Persians). Thorough straining is essential to all leathers which are to be freed from "stretch" as far as possible (*e.g.*, roller leather). A method of straining is sometimes used in which the skins are stretched

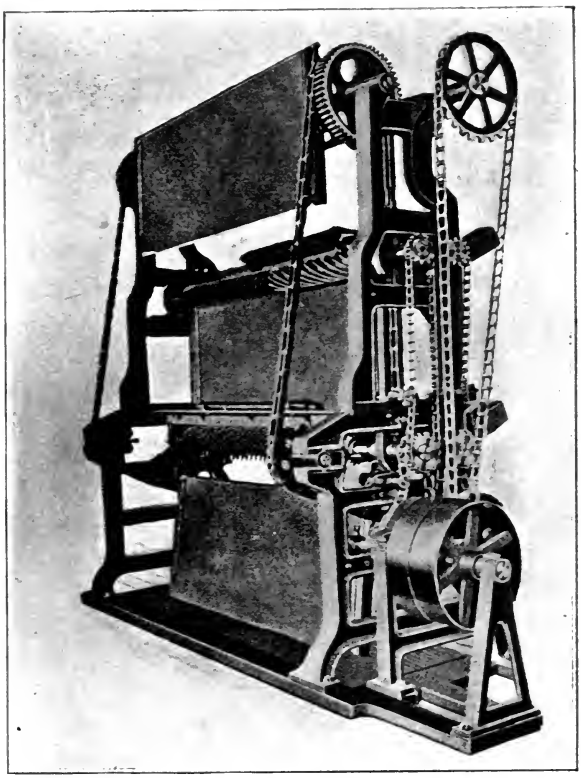


FIG. 95.—Serial table setting machine (Turner Co.).

out on a frame fitted with a wire gauze mesh.[1] The skin is held by toggles, which are attached to the mesh with hooks. Skins are also sometimes dried out on poles.

The finishing of dyed leathers is perhaps even more varied than the finishing of curried leathers, but there are several outstanding typical processes through which the goods may pass.

[1] Seymour-Jones patent.

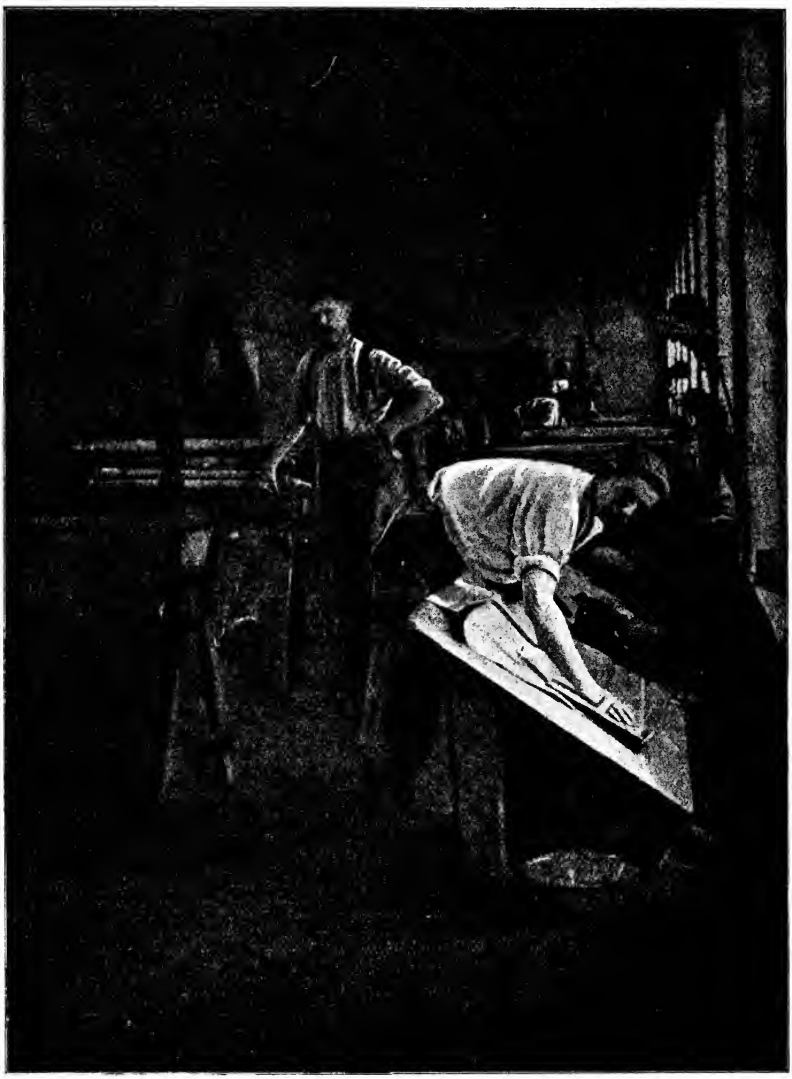


FIG 96.—Morocco finishing shop (Messrs. E. & J. Richardson, Newcastle).

Graining or boarding the skins consists in working up the grain pattern by pushing or pulling a fold in the skin by

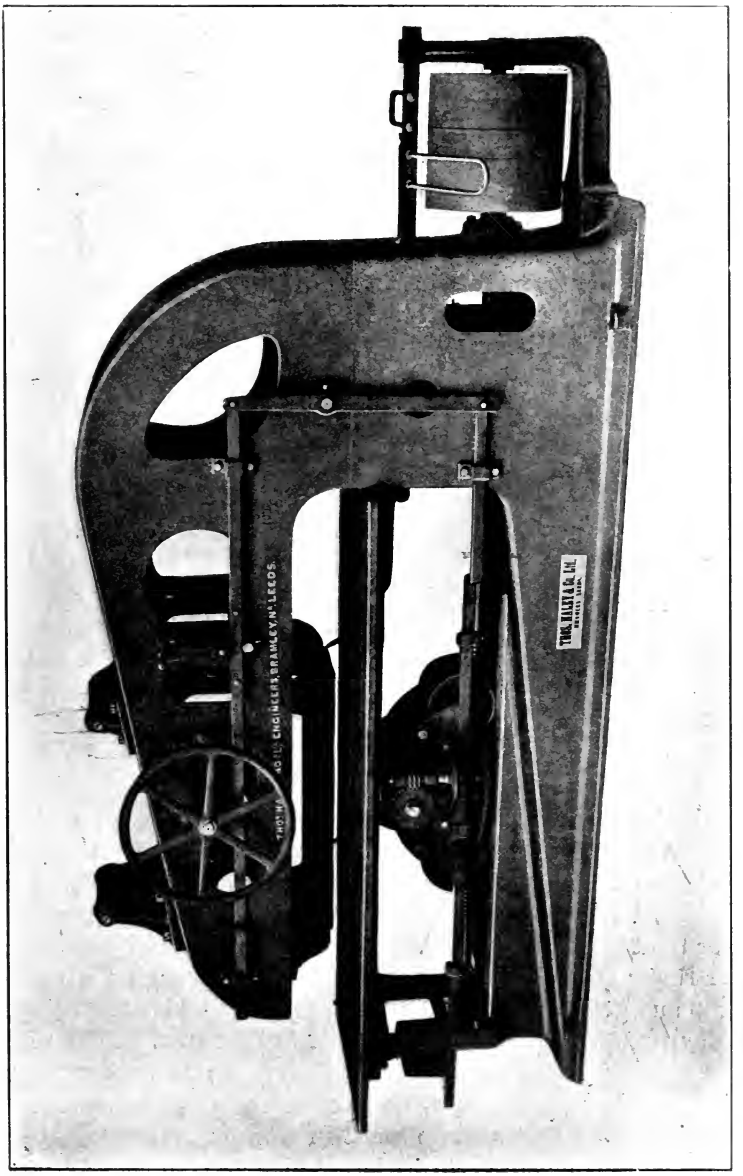


FIG. 97.—Embossing machine.

means of a cork board (Fig. 96) which grips or "bites" that part of the skin with which it is in contact. The skins are also "broken up" and softened by the process. This operation is one of skilled hand labour and offers great scope in producing different types of finish. The variation in size of the prominences and depressions yields "bold grains," "fine grains," and many intermediate stages. This is determined by the thickness and hardness of the skin and the pressure that is applied in graining and the nature of the board which is used. There is also great scope in producing "grains" of different shape. This is determined by the number of ways the skins are boarded, which may be anything up to seven, and also to a very great extent by the direction of the boarding, resulting in "hard grain," "straight grain," "cross grain," "long

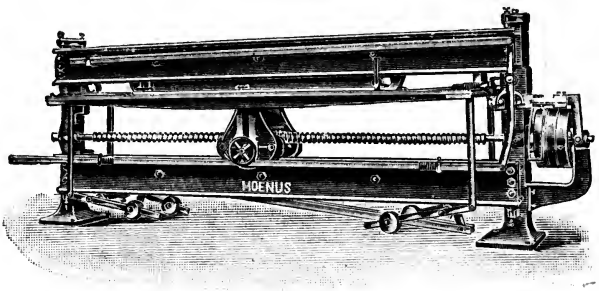


FIG. 98.—The "Altera" embossing machine.

grain," etc. In addition to the cork board there are rubber boards and "grippers" of ribbed wood and perforated tin, and the number and size of these ribs and perforations is a distinct factor in the size and nature of the resulting grain. For light goods the boards are held by the hand by a strap; for heavy goods by passing the arm right through the strap loop and grasping a handle.[1] The graining tables often slope away from the workman at an angle which varies largely with the class of goods. A leather "bolster" is also often used on the graining table, and some part of the skin is sometimes rolled up on a thin stick to assist in graining straight.

As pointed out in Chap. II., each hide or skin has its own

[1] This is called the "arm board."

characteristic grain pattern, and although this may be very considerably varied by the methods used in graining, the characteristic structure still remains as the basis of the result. In those cases where there is very little natural grain pattern, however, and in the cases of flesh splits where there is none, the grain pattern used as a basis of the finish may be stamped in by the leather dresser by "embossing" or "printing." Thus the characteristic seal skin grain pattern may be stamped into sheep skins or hide bellies for levant. One of the most recent embossing machines for this purpose is shown in Fig. 97, the

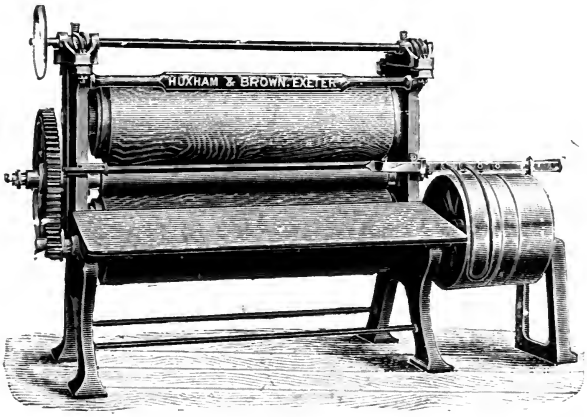


FIG. 99.—Printing machine.

impression being made by a steam-heated metallic box whilst the leather is in a damp condition. The surface of the leather is pressed up against the engraved box by means of a roller which travels underneath. Another popular embossing machine is shown in Fig. 98. In another type of machine, called "a printing machine," an engraved roller of considerable width is used along with other feed and nipping rollers, and the goods are fed through and embossed in one operation. The engraved roller may be replaced by other engraved rollers of different pattern, and these are all hollow inside so that steam may be passed through to heat them during the embossing process. In America an engraved plate is often used in a screw or hydraulic press. If an engraved roller be

substituted for a plain roller in some of the rolling machines and for the glass or agate of some of the glazing machines, a "printing machine" will result. With goods for which no elaborate or perfect grain pattern is desired, some pattern can be worked up by the "graining machines." These usually consist essentially of two rollers which rotate in the *same* direction. To these the folded skins are fed by a horizontal table, the top roller drawing the top layer of the fold through the rollers, and the bottom roller drawing the bottom layer of the fold away from the rollers. In this way the whole skin may be grained and softened.

Seasoning consists in applying dressing liquor which contains

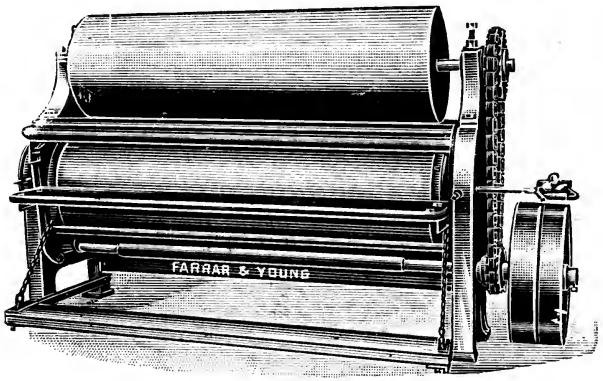


FIG. 100.—Graining machine.

albuminous and fatty matters. In the composition of seasons, milk, blood, blood albumen, egg albumen, and casein are the most common materials, the first being valuable because of the perfect emulsification of its fats. Glue and gelatin are also used in small quantities in certain cases. With dyed goods colouring matter is often added to the season to intensify or modify the shade ("flaming"), and with blacks, iron liquor, "inks" logwood, and coal tar blacks are often added. Linseed jelly, Iceland or Irish moss and other mucilaginous substances are also added to seasons and finishes to cover up defects and fill the grain. The season is in many cases a preparation for glazing, and its composition determines to a

large extent the appearance of the finish. Some goods are seasoned and brushed, but not glazed, by machine, and on the other hand, where a high glaze is required, goods may be re-seasoned and re-glazed until the required gloss has been obtained. Where waterproofness and fastness to rubbing are

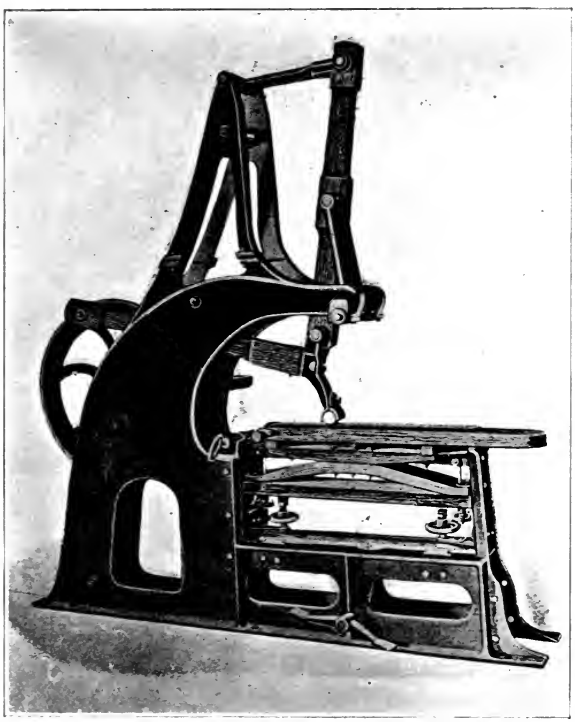


FIG. 101.—Level bed glazing machine.

important alcoholic shellac solutions are often applied before the final glazing.

Glazing is now practically always done by machine. There are many forms of machine for this purpose. The "hand-jigger" is one of the oldest types. It consists of an arm with a pendulum motion, which swings from an ordinary carriage spring or from a long ash pole attached to the ceiling. The bottom of the arm carries a cylinder of glass

or hardwood ("dummy") which is the glazing tool. This works along a bed of *lignum vitæ*, supported at each end, and therefore somewhat yielding. The leather is placed on this "bed" and changed in position by the left-hand whilst the right-hand moves the jigger. The cylinder is held in the jigger arm, and has only a very limited roll, hence by the friction a glaze is obtained. If a circularly-ribbed cylinder of box-wood replace the glazing tool it produces an impression of parallel lines ("tooth-rolling") which is a valuable assistance in graining. If an engraved roller replace the glazing tool

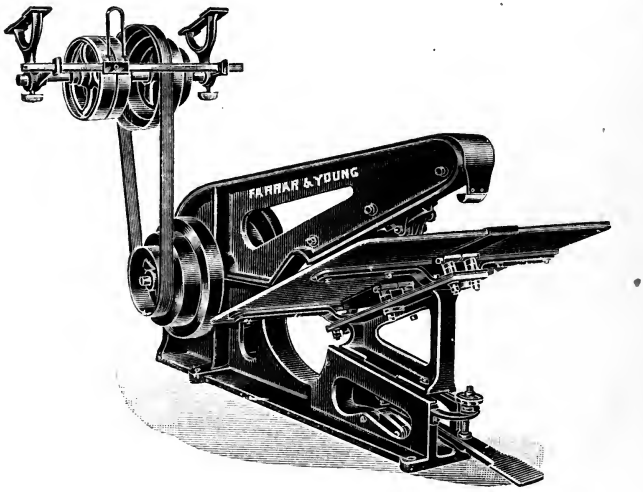


FIG. 102.—Glassing machine.

and be allowed to revolve the jigger becomes a printing machine. The "pendulum jigger" or "buck" is a similar machine, but worked by a crank with a long throw and attached to power. It is noisy, takes up much space, but does excellent work. Glazing machines should contain a liberal amount of wood in their construction. The modern type of machine is illustrated in Figs. 101, 102, and 106, the horizontal bed machine being used for skivers, Persians, basils, and for first glazing, and the inclined bed machine for chrome goods and second glazing. The tools are usually either of glass or agate. "Glassing" is a similar operation used chiefly on

curried goods, a slightly different type of machine ("grasshopper") being used.

Fluffing is another finishing operation which should be referred to here. This consists in subjecting the flesh side of the skin to the action of a rapidly-revolving emery wheel. The purpose of this process is to smooth the flesh side, to level the substance where shaving has been omitted, or to remove the

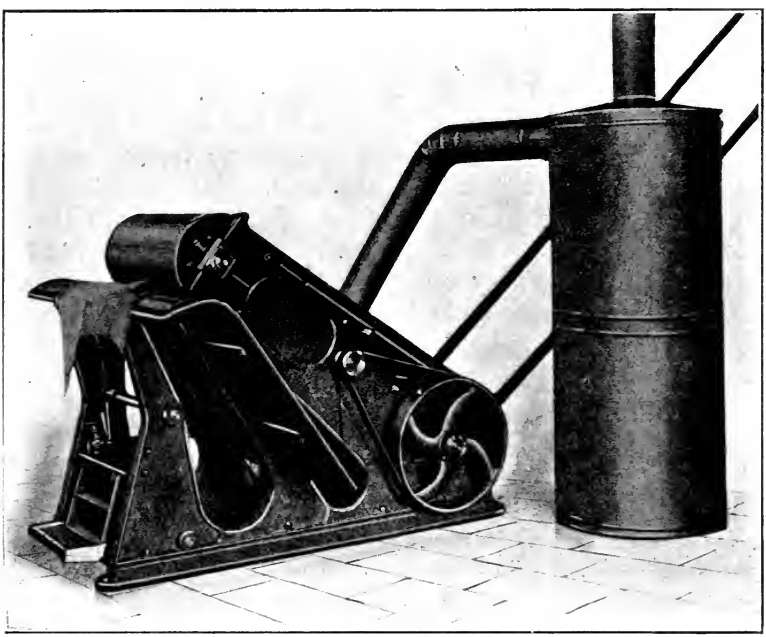


FIG. 103.—Fluffing machine (Farrar & Young).

marks of bad shaving, and also to raise a fine "nap" or downy surface. There are many kinds of machine, the chief variations being in the arrangement of the fan which should carry out the "fluff," and in the facilities for the interchange of "fine" and "coarse" emery wheels. The wheels may have the emery glued on, or may be covered with emery paper or cloth.

Brushing after seasoning, etc., is often done by hand, but also by machine. **Rolling** is used for smooth finishes, and is done by suitable machines.

It is obviously quite impossible to give the methods for finishing all types of light leather from even one kind of skin only, so that the brief outlines that follow are only to be taken as to some extent typical cases of light leather finishing.

Goat skins for morocco leather.—For "hard grain" moroccos the skins are first sorted according to their size, their colour, and the nature of their tannage. The larger and stouter skins are preferred for upholstery and the smaller for bookbinding and fancy articles. They are wet down in water at 50° C., and if fairly old are re-sumached. One to two pailfuls of sumach are used for every 10 dozen skins, and the goods should be run one and a half hours in the warm infusion. They are struck out for dyeing. If for bookbinding they are shaved before dyeing, if for upholstery, after dyeing. They are dyed with acid colours, and then put into cold water for a time. They are now folded belly to belly, flesh outwards, and horsed up to drain. After striking out on the flesh they are sammed quickly with only gentle heat. If for bookbinding they are hung up by the hind-shanks, if for upholstery they are nailed on the boards. After any necessary trimming they are seasoned with milk and water only, using 1 pint milk to 5 quarts water. This is well brushed or sponged over, and the goods laid grain to grain overnight. They are then tooth-rolled two ways, from left-hind shank to right-fore shank, and *vice versâ*. They are also sometimes tooth-rolled from belly to belly in addition, and piled again grain to grain. Pairs of skins are next taken, flesh outwards, and wet down by drawing through cold water and piling on the horse to drain. They are next "wet-grained" with a cork board in four ways, belly to belly, left-hind shank to right-fore shank, then across between the other shanks, and finally from neck to butt. The skins are now hung up and dried out in a hot stove to fix the grain. They are then softened by breaking down with a rubber board on grain and flesh. They are now "topped" with the milk and water season mentioned above,[1] adding a little colour and acetic acid if necessary. After hanging up for a short time they

[1] Or use ½ pint milk and 3½ ozs. albumen in 1 gallon water.

are then laid in pile, grain to grain, for a few hours, and then lightly brushed, piling now flesh to grain. A second thorough brushing is now given, and the goods are hung up and dried out in a warm stove. They are then broken down by graining three ways, from shank to shank, across, and from neck to butt, and are again thoroughly brushed.

A rather more elaborate method is carried out in the following way, taking the skins from the boards. They are seasoned with milk and water to which casein and albumen are sometimes added, dried somewhat and glazed. They are now superficially wet by drawing through water at 35° C., and left in pile or on the horse overnight. Graining now follows, and with the best goods this is done in seven ways, the object being to make the grain as round as possible. They are grained from belly to belly, shank to shank and across, keeping rather nearer to the neck or butt, then from neck to butt, then again from shank to shank and across, this time starting from the belly side of the shank, and finally they are grained right round to finish. They are now dried again; if for bookbinding, in a hot stove to set the grain and give a certain amount of stiffness; if for upholstery in a cool stove to ensure softness. They are now "flamed" with a little dye solution, dried, boarded on flesh and grain, topped with 5 parts albumen, 10 parts milk, and perhaps a little dye in 100 parts water, dried a little, and polished by brushing. They are then finally boarded and stoved.

For "levant" the dyed goods may be struck out, sammed, set, and dried out. They are wet back through cold water, dried a little, and wet grained four ways, belly to belly, shank to shank, across, and neck to butt, and then dried in a hot stove to firm and set the grain. They are now fluffed, and flamed if necessary. Seasoning follows, using 1 pint of milk in 6 quarts water, and brushing the solution well in. After airing off and trimming, the skins are glazed in the pendulum jigger, and grained up three ways, shank to shank, across, and neck to butt. After seasoning again and airing off they are glazed again and grained up. They are finished off by a very light pressure glazing and a final boarding.

For "black levant" the skins may be taken through the

following processes. After sumaching, striking out, samming, and setting, they are blacked with logwood and iron, and dried out in a hot stove. They are next drawn through cold water, drained, and dried till somewhat firm, and wet grained as described above for coloured goods. They are then dried out and fluffed. The season may contain blood, logwood, and iron. Either of the following will prove satisfactory: 10 ozs. logwood extract are dissolved in boiling water and diluted with cold to 3 gallons; 4 ozs. ferrous sulphate dissolved in cold water, 3 pints of milk, and 5 pints of bullock's blood are then added in turn, and the mixture made up to 5 gallons with water and mixed well; or 3 quarts logwood liquor are mixed with 3 quarts water, and ½ pint milk, ½ pint bullock's blood, ½ gill ammonia, and 1 gill of orchil are added. The season is thoroughly brushed on the grain, and the goods then hung up till ready for glazing, which is done in the pendulum jigger with heavy pressure. The grain is now thoroughly worked up again, and the goods dried off in the stove to set it. They are now glazed again with lighter pressure, and the grain once more drawn together. The goods are now oiled off with warm linseed or mineral oil.

Seal skins for morocco leather are treated somewhat similarly to goat skins.

For "black levants" the skins are damped down and struck out by machine. If for fine grain finishes they are split at this stage, but for larger grains they are merely levelled by shaving. If from a mixed tannage they are now scoured by hand. The skins are next lightly oiled with linseed oil and sammed stiff in a warm, damp stove. They are now set out by hand embossed with an engraved roller to assist in forming the grain of the size desired, and dried out to set it. They are now broken down, sometimes being wet back, and are then blacked. Where the natural grain is desired they are blacked immediately after setting, but are sometimes first seasoned. The logwood and ammonia infusion is first brushed on the grain and afterwards the iron solution. This latter nearly always contains glue, and may be made up in either of the following ways: ½ lb. good glue is dissolved in 1 quart water and 3 quarts iron liquor is added, or 2 lbs. of glue are soaked in 2 quarts iron

liquor till swollen and dissolved with the aid of heat. The glue gives a crisp feel to the finished goods, but the concentration used has considerable influence on the resulting grain, and in any case only a very light coat should be given with this liquor, and it should be brushed well in. After airing off, the goods are wet-grained four ways: belly to belly, shank to shank, across, and neck to butt, and then hung up by the butt

FIG. 104.—Currying seal skins (Messrs. E. & J. Richardson, Newcastle).

to dry out in a hot stove. After cooling they are fluffed. They are next seasoned with a solution of $\frac{3}{4}$ pint milk and $1\frac{1}{2}$ pints blood in 1 gallon of water. If the black is not good this may be diluted somewhat and a little nigrosine, corvoline, or naphthylamine black added to the liquor. The season is thoroughly rubbed in with a rather stiff brush, and after airing off the goods are glazed. After breaking down on grain and flesh with a rubber board the grain is again pushed up with a cork board, graining four ways as before. They are now dried

out in the stove and very lightly oiled with warm linseed oil. Fluffing may also be done after glazing.

For "colours" the skins are wet back and struck out as above, and split now if for fine grains. They are then scoured, dyed, set out, and shaved level where they have not been split. They are dried somewhat and grained from shank to shank and across with a gripper, and hung up by the butt in the stove to dry. They are again boarded, seasoned with milk and water only, and aired off. If dyed in dark colours they may be now very lightly coated with linseed oil. This facilitates the glazing which follows. They are then fluffed, regrained four ways as for blacks, and dried out in a hot stove. If necessary they are topped and brushed.

Basils for linings. The crust sheep skins are sorted, and soaked for shaving. They are shaved down the rig chiefly, to level the substance. The skins are then tumbled well in warm sumach, struck out well on the flesh with a brass slicker, nailed on the boards and dried right out. The "stain" is made up as follows in a bucket; 2 ozs. of starch are stirred well in $1\frac{1}{2}$ gallons of water and 2 tablespoonfuls of "Ruby Red" or other dyestuff added. The mixture is now well boiled, and finally 1 pint of milk is added. After staining with this, the goods are hung up from the neck, dried out, and glazed with a grasshopper machine. If the skins are a little hard they may be rolled up, and then softened by rolling with the hand board.

For fancy slipper work, etc. The crust skins are stained on the grain without wetting down and the dyes must therefore be very carefully chosen. The goods are first gone over with a starch of two parts dextrin, $\frac{1}{10}$ part ammonia in 100 parts of water, and are then dried and stained. After staining they are again dried, staked (p. 359), fluffed, seasoned, and glazed.

For legging and gaiter leathers they are finished on the flesh side. The skins for legging leather should be somewhat heavy. The crust skins are damped back, stretched, shaved and well sumached. They are then rinsed well in warm water, piled to drain and hung up to samm. They are next stained. A brown stain is common, and linseed jelly is usually

mixed with it to act as a filling agent. The stain is evenly coated over the flesh and gone over with a glass slicker, and the skins dried in a warm room. They are then wet back and stained again if necessary, and dried again. They are now broken up carefully with the "moon-knife" (p. 359) which raises a nap on the flesh but is apt to cause differences in the colour shade. For gaiter leathers they are dyed in paddle and flamed after samming, using linseed jelly. They are finished by fluffing over the emery wheel.

Skivers are finished for "paste grains" in the following way, and used for pocket-books, jewel-cases, cheap bookbinding, etc. They are sorted, wet back in water at 40° C., and "cleared" by placing for ten minutes in a very weak sulphuric acid solution, after which they are sweetened thoroughly by washing in several changes of clean water. They are dyed in paddle or tray as the drum is liable to tear them. They are then washed through cold water, dried on the horse, carefully struck out by hand on the flesh and "pasted," which consists in working over the flesh a size of glue jelly, about 10 per cent. strength according to quality. This is spread over the skin first, roughly, by hand, then evenly with a stiff brush, and afterwards smoothed over with a cloth. The goods are now dried off at only moderate heat for not less than twelve hours. If necessary they are now flamed with a $\frac{1}{2}$ per cent. solution of dye, dried again and next seasoned. This may be done with either of the following: 1 pint of milk in 3 pints of water, or 4 ozs. blood albumen are dissolved in 10 quarts water and $\frac{3}{4}$ pint milk are added. The skins are now dried further until in condition for printing. They are printed cross-grain, grained lightly from shank to shank and across, very lightly tooth-rolled with a No. 5 roller and glazed. They are now regrained two ways as before and dried out in the stove. They are now softened by breaking down over a sloping table with a graining board. Often they are sold in this condition, but sometimes are starched on the grain with a weak size which fixes the grain and gives a bright finish.

Another method of working up the grain is to dry from seasoning, tooth roll with a No. 4 roller two ways, from shank to shank and across, and roll off with the dummy.

They are now broken down with the graining board and sized off.

" Straight grain paste grains " are printed with the straight grain roller, the grain running from belly to belly ; they are now tooth-rolled three ways, from shank to shank and across with a No. 7 roller starting well on the belly side, and from belly to belly with a No. 4 roller. " Straight grains " not paste are dyed, flamed, seasoned, and tooth-rolled as just described, aired off and glazed.

For hat leathers the skivers should be good stout skins, and they are given a plain finish. They are wet down, sumached, lightly rinsed, and struck out. If for white or cream finishes they are now lead bleached. The dyeing which follows is always done in tray as a clean flesh is required. A good plan is to " bottom " first with a direct cotton dye at 45° C. and afterwards to " top " by staining (or dyeing) with a basic dye at 35° C., the basic dye forming a colour lake with the direct dye. For " browns " it is often usual to fix the tan with a titanium salt in paddle and then to dye in tray with a basic dyestuff. The goods are then washed immediately and paddled in sumach or oakwood extract to fix the dyestuff. After dyeing the goods are struck out, and a mucilage of Irish moss or a 1 to 2 per cent. solution of starch is applied and the goods then dried out on the boards. After a further application of a gelatinous mucilage the goods are rolled and finished.

Roans for " hard grains " are sumached, dried, seasoned, dried, and glazed. They are now drawn through tepid water and piled until in a suitable condition for printing with a hard grain roller. After wetting back and samming they are grained four ways, belly to belly, shank to shank, across, and from neck to butt. They are now dried at a low temperature, boarded flesh and grain, and aired off in the stove.

For " straight grains " the skins are grained from neck to butt or printed with a straight grain roller. They are then tooth-rolled as for straight grain paste grain skivers with No. 7 and No. 4 rollers, boarded flesh and grain, nearly dried and glazed. They are then boarded again and aired off in a cool stove.

Roller leather is required with a perfectly smooth grain,

quite devoid of stretch and with no grease. The sheep skins are very carefully sorted in the crust, soaked, rounded and shaved—generally by hand. They are then drummed in weak sumach and afterwards suspended in a liquor of oak bark and oakwood extract. The skins are next washed, well struck out on the flesh, sammed, and thoroughly set. If for a coloured finish they are stained now, pale yellow, golden brown, or orange being the usual colours. The goods are first prepared with a linseed mucilage, and the dry leather afterwards given three coats of a ½ per cent. dye solution. Sometimes, however, the mucilage is mixed with the dye, using 3 lbs. linseed to 10 gallons water, and adding ½ lb. dye. If they are to be finished in their natural colour, which is the case with the majority of them, they are merely seasoned with the linseed mucilage, with Irish moss or with other filling material. The skins are now dried in a thoroughly strained condition to take out all possible stretch. From the boards they are trimmed, seasoned with milk, linseed, and Irish moss, and after some little time rolled with a steel roller. They are then perched with the "moon-knife," fluffed, re-seasoned, stoved and glazed. Further sorting now generally takes place, and trimming to size. They are then short-haired where necessary with the moon-knife, re-glazed, ironed, and again sorted.

E. I. tanned sheep and goat skins are largely imported into this country and finished off for various purposes. They are tanned with turwar bark, a catechol tan, and cannot therefore be finished under the specifications of the Committee of the Society of Arts. They are often rather heavily oiled with sesame oil, and for most purposes should be degreased. The goods are sorted, soaked, and stripped in weak alkalies, usually soda, drumming twenty minutes at 35° C. They are then washed to remove excess of alkali and tannin and soured in ½ per cent. solution of sulphuric acid for five to ten minutes. This treatment may sometimes be omitted for black finishes. The goods are now drummed in sumach paste at 45° C. for an hour, using 1 to 1½ lbs. sumach per dozen skins

For moroccos the skins are now washed, struck out, dyed, dried strained, and trimmed. They are now wet back for

printing by brushing with warm water and piling overnight to equalise. "Straight grain" sheep skins are printed with a straight grain roller from belly to belly, boarded lightly from neck to butt, and dried out in a hot stove to harden the the grain. They are softened by boarding the grain, flamed with ¼ per cent. solution of dye, dried, seasoned with a good albumen finish, and tooth rolled with a No. 7 roller. They are now boarded three ways, shank to shank, well on the belly side, across, and from belly to belly, and then glazed. They are next re-boarded as before, lightly re-glazed, and again boarded. "Cross grains" undergo similar treatment, but are printed and boarded directly from shank to shank and then across. Goat skins for "levant" should be fairly stout skins; they are printed with a levant roller and grained four ways, from shank to shank on the belly side and across, and from shank to shank on the neck and butt side and across. They are then seasoned with milk, albumen and water, brushed and boarded from belly to belly and from neck to butt on flesh and grain, and then dried out in the stove. Black levants are similarly finished, boarding four ways, but are not printed.

For roller leather the light sheep skins should be chosen. They are trimmed, soaked, shaved on the back to level (often by machine), drum sumached, scoured, and dried strained. After further sorting they are stained, if for colours, dried strained, seasoned, and glazed. If finished in natural colour, they are seasoned, rolled damp, and dried out in hot stove. They are all now rounded, short-haired where necessary, ironed, and again sorted.

For linings the goods are fluffed, wet down in the tumbler, and lightly stripped. They are then washed and sammed, and are drummed in a paste of whitening for half an hour. Sometimes a little green or yellow dye is added to this paste. A fat-liquor of castor oil and soft soap is then added and the drumming continued for another half-hour. They are next horsed up for twenty-four hours without washing, and then hung up by the hind-shanks and dried rapidly. They are finished by boarding on the flesh from shank to shank and across, in order to soften. The goods may also be lead-bleached and dyed before fat-liquoring.

For glacés (colours) the skins are drum dyed and lightly fat-liquored or drum-oiled for ½ hour, using 1½ to 2 ozs. oil per dozen skins. They are then slicked out and dried. They are now machine staked (or perched), lightly fluffed and seasoned with one part egg albumen, 5 parts milk, and 100 parts water and possibly a little dye. If thought desirable, however, the dye may be omitted and the goods flamed with ½ per cent. solution of dye, and hung up by the neck to dry out in a hot stove. They are then glazed. If required soft they are perched and re-glazed. If a plain finish is required they are seasoned and rolled.

"Blacks" are sumached, often without clearing, and dyed with Induline. They are then fat-liquored and struck out. They are now drawn singly through a solution at 50° C. of 2 lbs. logwood extract, ½ lb. fustic extract, 2 ozs. (fluid) ammonia in 10 gallons water for 10 dozen skins, and afterwards through a cold solution of 2 lbs. ferrous sulphate and 4 ozs. copper sulphate in 10 gallons water, and are then immediately washed in water. They are now struck out, oiled with linseed oil and dried. After drying they are perched or staked, fluffed and seasoned. The season may be 3 ozs. logwood extract, ¾ oz. ferrous sulphate, 1 pint blood, 1 pint milk in 1 gallon water. The goods are now dried somewhat, well glazed, and oiled lightly on the grain with linseed oil.

"Blue-backs" are trimmed, fluffed, soaked, stripped and washed in drum. They are then dyed with 2 ozs. methyl violet per 10 dozen skins. After rinsing through cold water and draining, they are struck out and dried strained. Blacking the grain is now done with logwood and iron, and the skins are dried, seasoned, aired, glazed, perched, re-glazed and oiled off with linseed oil.

For bronzed leather (nursery shoe uppers, etc.), the sheep skins are stripped, cleared, lightly sumached, and dried strained at a high temperature. They are now perched, fluffed, and dyed an intense blue, deep maroon, or black, *e.g.*, naphthylamine black. They are now ready for the bronze stain which is a concentrated solution of a basic dye. A small coating of this is rubbed over the grain with a sponge. For

a gold bronze the liquor may consist of 5 parts magenta, 5 parts methyl violet, 5 parts gum arabic, in 100 parts methylated spirit. For a green bronze take 5 parts magenta, 2 parts diamond green, 10 parts of gum arabic in 100 parts methylated spirit. The goods are dried in a warm stove, perched, and seasoned with 5 parts ruby shellac, 10 parts glycerin in 100 parts methylated spirit. This is also applied with a sponge, and the goods are dried, glazed, and aired off. The shellac finish makes the colour fast to rubbing.

Hide splits may be dressed for common upholstery leather in the following manner: They are drummed in warm water, stripped and cleared if necessary, re-tanned in sumach or bright-coloured extract. They are next rinsed, struck out, drum dyed with basic dyes, and lightly fat-liquored. The goods are now drained, struck out, dried, softened by boarding, flamed, and dried out. They are now fluffed, rolled, and printed. If the goods are loose, flour is used along with the fat-liquor, and, if they are required firm glue may be added to the flaming solution.

CHAPTER XXV

THE FINISHING OF CHROME LEATHER

The finishing of the mineral- and combination-tanned leathers involves many of the mechanical operations previously described in connection with the finishing of the vegetable-tanned leathers, but includes also certain chemical and mechanical processes not yet fully discussed.

Neutralisation is the first operation after the tannage of chrome leather. It involves the removal of the superfluous tanning liquor, the "reversibly absorbed" free acid, and also a certain amount of hydrolysis of the chrome salt fixed on the fibre into a more basic salt which is retained, and a less basic and soluble chrome salt which is removed. If the soluble chrome salts are not removed they will form in fat-liquoring insoluble and sticky chrome soaps which make a satisfactory finish quite impossible. If the acid is not neutralised it will lead ultimately to tenderness in the leather, and the fat-liquoring is also upset by the liberation of free fatty acids from the soap that is employed. Although the removal of the excess of chrome salts and free acid can theoretically be brought about merely by washing, it is in practice customary to assist the process by the employment of weak alkalies, and hence the term neutralisation. The process is also hastened by the use of warm water, and hence the best, quickest, and most economical plan is to use first warm water for the removal of the bulk of the soluble salts, and afterwards to employ a bath of dilute weak alkali. The alkaline salts which may be used are borax, whitening, sodium silicate, sodium phosphate, sodium carbonate and bicarbonate. Whitening is the cheapest, but, being insoluble, it does not penetrate the leather, and therefore merely neutralises the acid which diffuses out, and is consequently very slow in its action. It is, moreover, not so easy to remove completely the

excess of it, and also the insoluble calcium sulphate which is formed when chrome sulphates have been used in tanning. Borax is, perhaps, the most widely used material, but the careful use of stronger alkalies, *e.g.*, sodium bicarbonate, has been found satisfactory in some factories. It is in any case clear, however, that the solution should be as dilute as possible in order to obtain even action throughout the leather, the real difficulty with strong alkalies being the roughening and tendering of the grain due to local over-neutralisation. With leathers of considerable thickness this difficulty is, of course, distinctly greater. After drumming in one or two changes of water at about 50° C., 1 to 3 per cent. borax on the weight of the tanned leather, after draining and striking out, may be employed for neutralisation, but the exact quantity will vary according to the amount of washing, the basicity of the tanning liquor, and the nature of the leather being manufactured. It is important for a good finish that any excess of borax or alkali should be thoroughly washed out.

Fat-liquoring is another process of great importance in the finishing of chrome leather, for although used originally with the dongola tannage, and afterwards applied to most other tannages, it has been found particularly useful for finishing the chrome-tanned leathers. It has already been mentioned that this process consists essentially in drumming the goods in an emulsion of soap and oil, which are both entirely absorbed by the leather, like the fats in drum stuffing. It is practically, therefore, a subsequent soap and oil tannage, and has indeed been used for the manufacture of leather from pelt which has not been otherwise tanned.[1] The amounts of grease used in finishing chrome leather are, generally speaking, much smaller than in the currying of dressing leather, but, nevertheless, vary very widely, from about 2 per cent. for glazed kid up to 12 per cent. for some heavily fat-liquored and dull-finished goods. The proportions of soap and oil also vary very greatly, according to their nature and the class of goods under treatment. Occasionally only a soap liquor is given and no oil or

[1] This method was used by the Aztecs of Mexico, and has been more recently utilised in the production of the so-called "napa" leather.

fat employed, and sometimes, *e.g.*, with chrome harness, the goods are first fat-liquored and then stuffed. The fat-liquoring process is of vital importance for the satisfactory finishing of chrome leather, and is also, perhaps, the most plentiful source of difficulties. The purpose of the process is to "feed" the rather empty chrome tannage, and give a certain amount of fulness, plumpness and softness. If, therefore, chrome leather is under-fat-liquored, it is liable to dry out hard, stiff and "tinny," and, on the other hand, if over-fat-liquored, it will be difficult to give a glazed finish to the goods. It is quite an essential for successful fat-liquoring that there should be a perfect emulsification of the soap and oil, for if not the distribution of the fats is liable to be very uneven, and give rise to a patchy appearance after glazing. The emulsion is made by dissolving the soap first in a small quantity of boiling water, then adding the oil and agitating the mixture thoroughly. The agitation is conveniently carried out on a small scale by the emulsifier of the pharmacists, which consists of a cylindrical vessel of tin and a perforated piston or plunger, which is worked up and down by the operator until the mixture in the tin cylinder is perfectly emulsified, which may be in fifteen minutes or more. On a large scale emulsifiers are used consisting of steam-jacketed pans, fitted inside with a screw or vaned axle which is rotated by power. The actual fat-liquoring process is best done in the hot air stuffing drum, and in a manner very closely similar to the stuffing of curried goods. The drum is heated, the goods drummed in it for a few minutes to warm them, and the fat-liquor then added through the hollow axle, and the drumming continued for three-quarters of an hour, or until the whole of the soap and oil are absorbed and nothing but a little dirty water is left. The temperature of fat-liquoring should be 50—55° C. for chrome goods, but is better under 50° C. for the vegetable tannages. Neats-foot, olive and castor oils are now usually considered the most suitable for fat-liquoring. The drying and semi-drying oils, and also the saturated oils should be avoided. Turkey red (sulphated castor) oil is sometimes used, but is liable to cause eventually the tendering of the leather. Soft (potassium) soaps are

generally preferred to hard (sodium) soaps, as the latter are more difficult to dissolve and tend to rather flat and hard leathers. The emulsification is often assisted by the addition of other materials. Egg-yolk is an excellent addition for this purpose, but it should not be added to the emulsifier until the temperature has fallen to 35° C.; degras and sod oil are sometimes used fairly liberally where dull finishes are desired. Casein and starch are also used to assist in emulsification, and the latter to give fulness. Sometimes free alkalies (*e.g.*, sodium carbonate) are used in the fat-liquor, and in this case not only is the emulsification of the oil helped, but these alkaline fat-liquors may also be used with leather in which the neutralisation has not been carried very far, or even, perhaps, omitted altogether. It is best to make up the fat-liquor just before use, but a good, well emulsified fat-liquor should stand for a week without separating out. It will be clear from what has been said that if too large a quantity of oil or too small a quantity of soap be used, the oil may separate out in the operation and deposit on the surface of the leather and in the drum. This may also be caused by using a neutral fat-liquor with imperfectly neutralised goods, and also by too low a temperature. The remedy is to heat up and continue the drumming with more soap and alkali. Whether goods should be fat-liquored before or after dyeing, is a question for discussion in any particular case. The disadvantages of dyeing after fat-liquoring is that distinctly more colouring matter is needed, and that there is a tendency to blotchy results. The disadvantage of dyeing before fat-liquoring, is that the alkaline fat-liquor is very liable to affect the colour of the dyed goods, and make it therefore practically impossible to dye to shade. A point to be remembered in this connection is that chrome leather must not be dried out completely after tanning, for it will not wet back again, and hence the useful "crust" stage does not exist for this class of goods. Lamb proposes to overcome these difficulties by giving a special light fat-liquor, then drying out to crust, sorting, wetting back in hot water, dyeing and then giving a further fat-liquor where necessary.

Staking and perching are also processes belonging chiefly to the mineral tannages. They have both for their aim the

softening of the leather which has dried or nearly dried out in a somewhat harsh, stiff and non-pliant condition. In staking the goods are worked vigorously over a semi-circular blade of blunt steel fixed vertically at the top of a wooden post. In perching the mechanical treatment is less violent, the goods being fixed on a "perch"—a horizontal pole about 5 feet above the ground—and scraped by means of the "moon-knife," a circular and slightly concave knife of about 9 inches

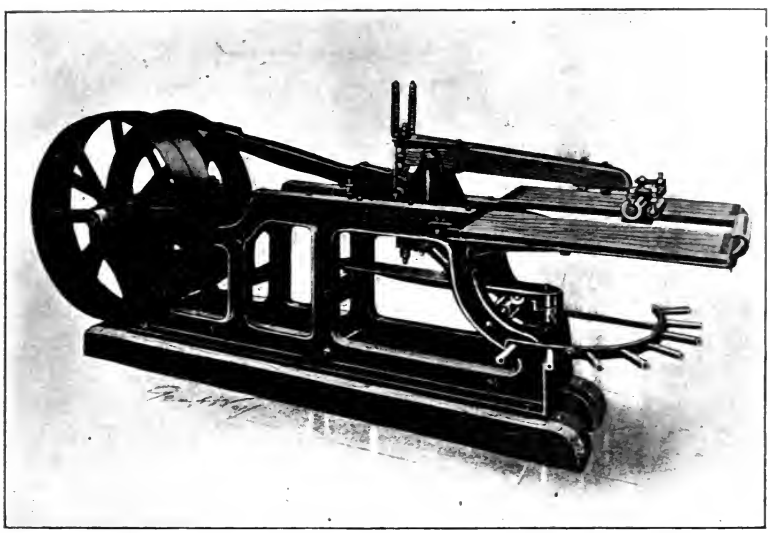


FIG. 105.—Slocomb staking machine.

diameter with a central hole of about 4½ inches diameter, or by means of the "crutch stake." This operation is one of hand labour and requires some care and considerable skill. Staking is now done extensively by machine, the Slocomb machine (Fig. 105), being very popular for this purpose. The machine head, which does the actual staking, consists essentially of two rollers between which is fixed the staking blade. The rollers are on one side of the leather and the blade on the other, and the leather is held whilst the machine head moves. The position of the leather is shifted by the hands, and the pressure adjusted by the knees of the operator.

Box calf, the most popular form of chrome calf, may be finished in the following way. The goods are laid in pile overnight and then washed in two changes of water at 50° C. and neutralised with 3 per cent. borax on the pelt weight. drumming half-hour or more. The skins are then again washed well in cold water. They are now well struck out, hung up to dry somewhat, and when in a properly sammed condition are shaved by machine and weighed.

Another mode of procedure is to wash in warm water, strike out well, and then samm for shaving. After machine shaving they are weighed. They are neutralised with 2 per cent. of borax on the leather weight in 1 per cent. solution immediately before dyeing and fat-liquoring. By this method there is less danger of the further diffusion of acid or chrome salt causing difficulty in the fat-liquoring.

By whichever method the goods have been treated the next process is that of dyeing and fat-liquoring. This may be done in many ways, but perhaps most usually by the joint use of logwood and a coal tar black. Quantities are calculated on the shaver's weight, and all percentages now given have reference to 100 lbs. of sammed and shaved leather. The dye solution may be made up of 1 to 1½ per cent. of "Chrome leather black C" (Casella); ¼ per cent. solid logwood extract in 4 to 4½ gallons per cent. water. The goods are warmed in the hot drum to 50° to 60° C., and the dye solution at the same temperature gradually run through the hollow axle whilst the drum is in motion. The drumming is continued for 30 to 45 minutes. The fat-liquor is now run into the drum, after perhaps running off about half of the dye liquor which remains. The fat-liquor may consist of 2 per cent. soft soap, 2½ per cent. neatsfoot oil, and 1½ per cent. of degras —well emulsified. The drumming is continued another three-quarters of an hour, and the goods horsed up overnight. When the proportion of aniline black is decreased and the amount of logwood increased, the goods are often folded and dipped through a "striker" of iron and copper sulphates.

The skins are now well struck out and dried out, hanging up by the hind shanks. They are wet back for staking by leaving in damp sawdust for 36 to 48 hours. Staking now follows in the

Slocomb machine, and the goods are next dried strained at 40° C. and are then ready for finishing. They are sponged over first with a 10 per cent. solution of lactic acid seasoned with a milk and blood solution to which aniline black or logwood and iron have been added. The following will give good results: 10 ozs. logwood extract are dissolved in boiling water, diluted somewhat with cold, and a solution containing 4 ozs. ferrous sulphate is added; 3 pints of milk and 5 pints blood are also now added and the mixture made up to 5 gallons and well mixed. When surface-dry the goods are glazed. They are now grained two ways, from neck to butt and from belly to belly. This is often done by machine. After re-seasoning, drying out, and again glazing they are boarded lightly to bring out the grain, oiled off with mineral oil, trimmed, sorted and measured by machine.

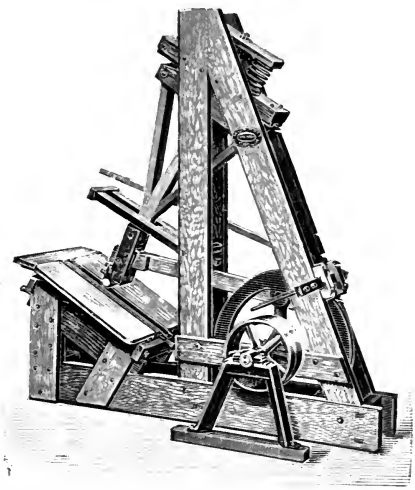


FIG. 106. — Bower's chrome glazer (Huxham & Brown's).

This process may, of course, be modified in many ways. The blacking may be done by logwood and iron, and this may follow the fat-liquoring instead of preceding it. Another way also is to drum dye a blue-black with induline or nigrosine, then to fat-liquor, and afterwards give a black stain with an aniline dye or with logwood and iron. The goods also may be staked before drying out completely, and if so this should be done when nearly dry. They may also be re-staked when quite dry or after glazing. Where a fine grain is desired the goods should be grained before glazing whilst damp with seasoning and then re-grained after the final glazing.

Box calf imitations are made from E. I. kips ("box kip") and split hides ("box sides"). They are chrome tanned and

finished as for box calf, but after staking damp the kips are sometimes printed or embossed with the "box" grain, so that on boarding the well-known box calf grain works up well.

Glacé calf receives nearly the same process as box calf, but the graining is omitted and the goods are seasoned and glazed three times. Small skins are mostly used for this class of goods.

Dull calf (plain) is also finished in much the same way, but is well fat-liquored with degras and neats-foot oil. The goods are stained, not dyed, and are ironed by hand, sized with a mixture of gum arabic, olive oil, soap and logwood, brushed by machine, dried and rolled off.

Heavy chrome butts for somewhat heavy and waterproof leather (golf and shooting boots, etc.) are grained and finished dull. They are typified by the "Zug" and "Beva" leathers. The goods are neutralised, sammed by machine, or struck out and fat-liquored with 2 lbs. neats-foot oil, 2 lbs. soft soap per 100 lbs. sammed leather. They are drummed about half-hour in the fat-liquor, drained and sammed for shaving, which is distinctly easier after fat-liquoring. They are blacked on the table only on the grain side. A solution of 5 parts logwood extract, 1 part fustic extract, and possibly a little ammonia in 100 parts water is brushed on the grain, and after a little while a solution of 3 parts ferrous sulphate, ½ part copper sulphate, in 100 parts water is brushed over, and after a short time the goods are brushed with warm water and hung up to samm. They are now re-fat-liquored by brushing on a liberal coat of a concentrated emulsion on the grain. For this purpose 5 lbs. neats-foot oil, 2 lbs. soft soap, and 5 egg-yolks are emulsified in 6 gallons water. The goods are horsed grain to grain for twenty-four hours at least to "feed," and then dried, hanging up by the hind shanks. The leather should now be quite soft and require no staking. The goods are often perched, however, and they are then grained in three directions to give a somewhat round grain. They are first "double-quartered" and then "run to length." A finish is now applied, consisting of 2 ozs. beeswax, 4 ozs. soft soap, 4 ozs. neats-foot oil and 1 quart water. This is applied hot to the grain and the goods laid up for 2 to 3 days. They are now finished by brushing and sometimes oiled off with linseed oil or a mixture of linseed and mineral oils in equal proportions.

Willow calf may be taken as a representative finish for coloured chrome calf. The goods are neutralised with borax as for box calf and then mordanted with a dilute solution of sumach extract, or with a filtered sumach leaf infusion. The skins are drummed in this liquor at 50° C. for about half an hour, and the tannin is then fixed by the addition of 4 ozs. tartar emetic per dozen skins, and the drumming continued for another half-hour in the same liquor. After washing and striking out the goods are next dyed in drum at 60° C., adding the basic colours gradually and drumming in all about three-quarters of an hour. The fat-liquor is next added gradually to the goods in the same drum. It may consist of ½ per cent. castor oil soap or olive oil soap and ¾ per cent. castor oil The skins are now horsed up for an hour, dipped through water at 60° C., struck out and hung up to dry (or dried strained). They are then wet back by leaving in damp sawdust for thirty-six hours and staked in the Slocomb machine, dried somewhat and re-staked. They are seasoned with milk, albumen and water only, dried and glazed. They are then re-seasoned and re-glazed, and finally grained one way, from neck to butt. When a fine grain is desired they should be grained also before the first glazing, and they are now often grained two ways, like box calf.

A method useful for browns, reds, etc., is to fix the tannin mordant with titanium salts, which give colours very fast to light and also reduce the amount of dye required. The dye-woods are also very useful both for mordanting and giving a ground colour, and titanium salts may be usefully employed with them for fixing. The direct dyes may be also used without a mordant and are useful for giving pale shades.

Another way of finishing is to dye after fat-liquoring. The goods are neutralised as before, struck out by machine, fat-liquored, shaved and weighed. They are then dyed at 60° C. Acid colours may be used along with sodium bisulphate, and the goods washed in warm water, struck out, and dried strained. They are then staked and finished as usual. Linseed and other mucilages may be mixed with the season if thought desirable, *e.g.*, the season might be made by boiling ½ lb. linseed in 1 gallon water, straining, and adding 2 ozs. albumen when cooler

Glacé kid (black) is a typical chrome light leather. The American factories lay considerable stress on the neutralisation. The goods are taken from the hypo bath, struck out thoroughly by machine, and neutralised with 1 per cent. borax for several hours, and then washed in paddle, often for many hours, in running water. They are then again struck out by machine and lightly shaved. Considerable time, power, and water are used in this method, and it is probable that, with care, equally good results might be obtained with washing in tepid water or in running water for some hours, striking out by machine, shaving and neutralising with 3 per cent. borax on the shaved weight by drumming for one hour only at 45° C., and afterwards washing in drum for half an hour in clean water.

Blue backing now follows, the skins being drum dyed blue with a coal tar colour, *e.g.*, acid violet 6 B.,[1] using 10 ozs. for every five dozen skins, and drumming half an hour at 45° C. They are now struck out and blacked on the grain with logwood and iron. This may be done by brushing over the solution in the ordinary way or by pairing or pleating the skins and passing them rapidly through vats containing the solutions. If the latter method is adopted there may be three solutions, the first containing 3 ozs. ammonia in 60 gallons water and used at ordinary temperature, the second being at 45—50° C., and containing 5 lbs. logwood extract and ½ lb. fustic extract in 60 gallons water, and the third, used at ordinary temperature, containing 5 lbs. ferrous sulphate, 5 ozs. copper sulphate in 60 gallons water. A pack of five dozen skins may be passed through these liquors without their being strengthened, but the goods must be well washed in warm water immediately to remove the excess of iron salt. The staining may also be with aniline blacks. Another method often used is to omit the blue-backing and to dye black immediately with logwood and iron. For every 100 lbs. shaved leather, 3 lbs. logwood extract, ¼ lb. fustic extract, and 1 oz. (fluid) ammonia are dissolved in 15 gallons water, and the goods drummed in this for three-quarters of an hour at 45° C. Three-quarters of the liquor is now run away and 4 oz. (fluid) iron liquor in 10 gallons water are added,

[1] Methyl violet, methylene blue, or nigrosine may also be used.

and the drumming continued for a few minutes only, when all the liquor is run off and the goods drummed in running water for one hour to remove excess of iron.

Whichever method has been employed the goods are struck out and sammed for fat-liquoring. The skins are then drummed ten minutes in a hot, dry drum, and the fat-liquor added at 55° C. This may consist of 2½ lbs. neats-foot oil, 1 lb. soap, and ¾ lb. egg-yolk for every 100 lbs. leather. The goods are drummed three-quarters of an hour, the liquor run off, and the goods drummed dry with the door off to cool and distribute the fat-liquor. The goods are then horsed up overnight, struck out, painted with a 5 per cent. glycerin solution, hung up over poles, and dried rapidly at 30° C., taking about five hours. They are then wet back for staking by leaving in damp sawdust for about thirty-six hours. They are staked first in the Slocomb machine on the neck and butt only, and then by hand over the beam, and finally perched with the moon-knife and pulled into shape. The goods should be somewhat drier after each of these operations. The exact condition of dryness in these staking processes is a matter of considerable importance; if staked too damp the leather is tinny, if staked too dry the full stretch and pliability cannot be obtained. In finishing they are first fluffed (if desired) and then seasoned. The season may be made thus: 5 ozs. Corvoline B are dissolved in boiling water, and, after cooling, 3 parts milk and 5 parts blood are added, and the whole made up to 5 gallons with water. The logwood season (p. 361) may also be used. If over fat-liquored the grain may be sponged over with 10 per cent. lactic or acetic acid solution before seasoning. When dry the skins may be glazed twice round with glass, and after re-seasoning glazed twice round with agate. They are then staked, re-glazed, and finally oiled off with a mixture of linseed and mineral oil in equal proportions, and sorted according to quality, size and thickness.

Dull kid differs in its finish from glacé chiefly in the much heavier fat-liquor which is given to it. They are staked as for glacé goods, but instead of glazing are ironed by hand and oiled off.

Coloured glacé kid.—After neutralising and washing in the

same way as for blacks, they are mordanted with a dyewood extract. About 2 ozs. of extract are used for each dozen skins, and the goods are drummed in the infusion for half an hour at 45° C. Peachwood extract gives a claret red colour, and is used where reds and ox-blood shades are desired; fustic extract dyes a lemon yellow, in conjunction with gambier a pale fawn, and is used for the production of browns. For dark browns some logwood extract may be used with the fustic extract. Palmetto and hemlock extracts are also used, giving a pinkish fawn and red colour respectively. The tannin mordant is fixed with antimony or titanium salts, and the skins then fat-liquored. The fat-liquor consists of 3 lbs. soft soap, 3 lbs: neatsfoot oil, and 5 egg yolks, in 10 gallons water for each 100 lbs. leather. After drumming with this for half an hour the dye is added to the drum without stopping it. Where acid colours are employed, the colour acid should be liberated by means of formic acid or sodium bisulphate in order that the fat-liquor may not be affected. Half the quantity of dyestuff should be added at first, and after ten minutes' drumming the acid or bisulphate should be run in, and in another ten minutes the rest of the dyestuff. The drumming should now be continued for three-quarters of an hour. For fancy shades the fat-liquor should not contain soap, but should consist of egg yolk only. The goods after dyeing are laid in pile, hung up to dry by the hind shanks or over poles. They are then damped back, staked, and seasoned with 5 parts milk, 3 parts egg albumen in 200 parts water. They are next glazed, fluffed, staked, and re-glazed.

Imitation glacé kid from sheep skins is finished in much the same manner as glacé goat. For shoe leathers a certain amount of firmness must be retained, and as the skins are naturally soft and porous only a light fat-liquor should be given. If from a one-bath tannage, they are horsed up to drain twenty-four hours and then neutralised with 2 per cent. borax for half an hour, and washed for one hour in running water.

If for blacks they are given a slight re-tannage in gambier to make them less stretchy; they should be paddled half an hour in the liquor, using 2 lbs. gambier and 6 gallons water

for each dozen skins. They are next paddled half an hour in a logwood liquor. This consists of ½ lb. solid logwood extract, 2 ozs. fustic extract in 6 gallons water, for each dozen skins. The striker is then added to the same liquor consisting of 1 oz. ferrous sulphate and ½ oz. copper sulphate, and after running ten minutes the skins are washed in clean water for a quarter of an hour. They are then lightly fat-liquored, horsed up overnight, set out, oiled, and hung up by the shanks to dry out. They are wet back, staked, and dried strained. After trimming they are seasoned, dried, glazed, and then re-seasoned, dried, and re-glazed, finally oiling off lightly.

If for colours they are mordanted with fustic or sumach, fixed with antimony salts, and dyed with coal tar colours. They are then washed, struck out and fat-liquored with ½ lb. soft soap in 2 gallons water for a dozen small skins. For the same number of skins 1 pint egg-yolk and ½ pint olive oil make a good fat-liquor, and may be used at 30° C. The skins are again struck out, oiled very lightly on the grain with sperm or neatsfoot oil, dried strained, staked and finished.

For glove leathers, flour may be used in the fat-liquor, and it is in any case better to choose those skins which were tawed before chroming by the one-bath process. In this case if egg-yolk, flour, and oil have been used, no fat-liquor is given. It is generally considered essential to degrease by pressure in the limed state in order to obtain a good glacé finish on sheep skins.

Chrome chamois from sheep skins splits may be finished for lining purposes in the following way. The goods are sammed by setting out and weighed. They are then washed in warm water, neutralised with 1 per cent. soda in ½ per cent. solution, and washed off in cold water. They are then fat-liquored at 50—60° C. with 3 per cent. soap, ½ per cent. soda, and 2 per cent. egg yolk. They are horsed up overnight, set out and dried out. After damping back in sawdust they are staked two or three times till dry and finally fluffed. If not sufficiently soft the skins may be wet back in hot water, worked about whilst wet, and again dried out with staking. When the goods are to be used for fancy purposes they should be dyed also whilst fat-liquoring.

Picking band butts are finished in many ways. The quantities given here refer to the pelt weight. After cutting down the back the goods are drummed in water at 60° C. for twenty minutes and neutralised with 1 per cent. borax, and then sammed for fat-liquouring or stuffing by a hydraulic press or a samming machine. The fat-liquor may be any of the following: 10 per cent. cod oil, 3 per cent. tallow, 10 per cent. hard soap; or, 7 per cent. cod oil, 3 per cent. tallow, and 6 per cent. hard soap; or, 7 per cent. degras, 3 per cent. tallow, and 3 per cent. soap. The drumming should be somewhat prolonged. The goods are now hung up for a time and then set out by hand, covering the grain with French chalk after striking to improve the colour. The goods are then dried out, left in pile a few days, slicked out again and softened in special machines. These may either be on the principle of the Continental boarding machine or may consist of a grooved press. The bends are then cut into picking bands of the required width.

Another way of finishing sometimes used is to nearly dry out after fat-liquouring and stake several times by machine until quite dry. The flesh is then lightly shaved to remove the roughness caused by staking, and both sides are dusted with French chalk and wiped with a clean cloth.

Harness backs are curried after a light fat-liquoring. The goods are neutralised, sammed by machine, and fat-liquored with $4\frac{1}{2}$ per cent. soap on the sammed weight. They are then well set out by machine, oiled heavily on the grain with mineral oil, and hung up to samm further till ready for stuffing. This may be done by hand, in the drum, or by burning-in. In drum stuffing the greases should be carefully chosen, stearin or pressed tallow being used in the greatest quantity, together with small amounts of sod oil and wool fat. Where the burning-in process is used the samming is brought about whilst the backs are stretched on special frames, and is continued until they are almost completely dry. The greases in which the goods are immersed are paraffin wax and ceresin wax, let down by mineral oil. The goods should remain in the melted mixture rather over half an hour at a temperature about 10° C. higher than the melting point of the grease

mixture. They are then drained for a few seconds, quickly slicked out and laid in pile to cool in a flat condition. They are then cleaned, blacked with lamp black and oil, glassed well and back-tallowed on the grain. If the goods are plunged into cold water after burning-in, a mellower but more stretchy leather will result. Good brown harness cannot be easily obtained, and the chrome black harness is more fitted for rough usage than for cases where polish and appearance are important.

Strap butts on coming from the last liquor are left in pile for twelve hours to drain, and then thoroughly set out by machine. The goods are now washed in pits for two days, using plenty of water, the leather being set out once or twice in the process. The method of washing in tepid water and neutralising in drum should be avoided. The butts are not fat-liquored either, but oiled with heavy mineral oil (often containing vaseline) and stretched thoroughly on powerful stretching frames. During this process the goods are slowly dried and the flesh side is coated with a mixture of degras and vaseline, to which a little wool fat may be added. This coating should not be too freely applied, and the butts must on no account be taken from the frames until thoroughly dry. They are heated to 45° to 50° C. to make permanent the effect on stretching. They are finished by fluffing the flesh, rolling heavily by machine, and applying French chalk to flesh and grain.

Motor butts (for tyres) are lightly fat-liquored with soap only, set out, sammed, machine boarded, lightly set out, dried further, and finally re-boarded by machine, dried out, and French chalked on flesh and grain.

Sole butts are first neutralised by drumming with ½ per cent. borax on the pelt weight for half an hour at 40° C., and the soluble salts then removed by washing. The butts are then thoroughly set out in the Turner drum machine, oiled with mineral oil or fat-liquored and hung up to samm. When highly sammed they are set out again, dried out very slowly, rolled, and French chalked. They are now cut up into bends. A two-bath tannage is generally preferred for this finish, better colour being usually obtained. The goods are employed for tennis shoes and similar purposes.

Chrome sole leather for ordinary boots is heavily staffed with greases, but chiefly paraffin wax. It has a most unfortunate tendency to slip in wet weather. This tendency is said to be overcome by immersing the goods when dry for a quarter of an hour in a melted mixture of one part resin and two parts tallow. They are then slicked out quickly, French chalked, and piled to cool.

CHAPTER XXVI

THE FINISHING OF THE ALUM- AND COMBINATION-TANNED LEATHERS

Glove kid may be dyed and finished by the following methods. The goods are first carefully but thoroughly wet back in a small quantity of water at 35° C., being sometimes trodden in tubs with the bare feet. They are then drummed in another quantity of clean water at 35° C. for a quarter-hour to distribute the moisture evenly throughout the goods. They are next drawn through tepid water, and are ready for dyeing.

If the skins are to be brush dyed they are first "re-egged" to replace the tawing materials lost in soaking. For 100 medium-sized skins (each weighing 2 to 3 lbs. after soaking) 2½ lbs. preserved egg-yolk and 2½ lbs. salt should be used, and the goods drummed with the mixture for one and a half hours and then laid in pile for twenty-four hours. Sometimes flour replaces salt, and occasionally flour and alum are used in addition. The goods are now slicked out on the table with a vulcanite slicker, and are mordanted and dyed with the natural dyes. For the mordant solution a weak alkali is employed. Stale urine was once much used for this purpose, but is now largely replaced by weak solutions of ammonia (0·1 per cent. strength), potassium carbonate, soft soap, and sodium silicate. The mordant solution is first brushed on, and afterwards a 3 per cent. solution of a dyewood extract. These dyewood colours have the advantage of preventing the "gaping" or "grinning" of the finished leathers, *i.e.*, their showing white undyed portions when stretched. The tannin they contain also assists in the glossy finish, but too much should not be present in the infusion, or the grain will be tightened and rendered harsh by its retanning effect, and the stretch of the leather will also

be seriously impaired. Methylated spirit is often added to the dye solution to prevent frothing with the egg-yolk in the skin. A " striker " of a solution of some metallic salt is often also subsequently applied to modify the shade; ferrous sulphate, copper sulphate, zinc sulphate, and potassium dichromate being commonly employed for this purpose. Topping with a basic coal tar dyestuff is now usual, and the use of these colours is slowly increasing even for bottoming. The skins are now slicked out with a brass or vulcanite slicker and dried in a well-ventilated room. They are then damped back in wet sawdust, staked, pulled into shape over a hurdle, fluffed, nearly dried out and re-staked. They are now seasoned with a weak solution of albumen or gum arabic, sammed brushed, and ironed with a warm flat-iron. They are then dusted on the grain with a small quantity of French chalk and brushed off by machine. A wax finish of 2 parts soft soap and $\frac{1}{2}$ part of wax in 100 parts water may also be used; after applying this finish the goods are dried and rubbed with flannel.

If the skins are tray dyed this is done before re-egging, but this method is only suitable for very small quantities of skins. The drum method of dyeing is, however, more suitable and is becoming increasingly adopted. The skins are soaked by drumming in water at 35—40° C., and after running off the liquor the " bottom," a natural dye, is added. Fustic and turmeric are suitable where yellows and browns are desired and may be saddened by the addition of iron, chromium, or copper salts. The goods are drummed half-hour with the natural dye, and the coal tar colour for topping may then be added and the drumming continued until the required fulness of shade is obtained. The greater part of the liquor is now run away and the re-egging mixture of egg-yolk and salt is added, and the drumming continued for quarter-hour. The goods are now left to drain for a time, dried out slowly, and finished as before. Another method is to drum half-hour with a solution of 4 lbs. chrome alum for every 100 lbs. wet leather, and to dye with the acid coal tar dyestuffs and sodium bisulphate. In this case also the dyewoods may be employed for bottoming.

Blacks are always obtained by means of logwood and iron. A 3 per cent. solution of logwood extract and a 2 per cent. solution of ferrous sulphate are used. Where drum dyeing is used, 5 per cent. logwood extract and 1 per cent. fustic extract on the weight of the soaked leather should be used, drumming the goods half-hour in the liquor. Three parts of the bath are now run off, a solution of $\frac{1}{2}$ per cent. ferrous sulphate on the leather weight is added, and the drumming continued for a few minutes longer. The goods are then washed well in warm water to remove excess of iron, and are now re-egged and finished. The season may consist of 1 part oil well emulsified with 2 parts of soap in 50 parts water to which $\frac{1}{8}$ part of potassium dichromate has been added. This is sponged on, the goods are dried, lightly coated with linseed oil, ironed, re-oiled, dried out and brushed.

Whites are dressed by re-egging as usual by the addition of 10 lbs. of French chalk per 100 skins. The goods are allowed to lie for a time in the drum when the operation is completed, and afterwards struck out and dried.

Calf kid is finished dull and black, but otherwise in a somewhat similar way to alumed gloved leather. Staking and shaving are first necessary if these operations were not carried out before ageing, which latter way is the better plan. The skins are re-egged before blacking, which latter is done with the brush. They are then dried out, softened by grounding with the moon-knife, and then by staking or perching. A soap and wax finish is given of 1 lb. curd soap, $\frac{1}{2}$ lb. beeswax, 2 ozs. nigrosine and 1 gallon water. This is well rubbed over and the goods ironed and lightly oiled with olive oil. They are sometimes "glossed" with a wax polish, rubbed well, and French chalked.

Glazed dongola goat may be taken as representing the dongola tannages. The skins are fat-liquored and rapidly dried out in a well-ventilated room. They are then damped back in sawdust, shaved on the neck by machine, staked, fluffed, and blue backed with methyl violet. They are now tray-dyed black with logwood and iron and dried out on poles at a moderate heat. They are next damped back, staked or perched, brushed, seasoned, dried, and glazed. They are now

re-seasoned and re-glazed until the required gloss has been obtained, staking between the glazings.

Dull dongola is more heavily fat-liquored and the skins are ironed and oiled off after seasoning, instead of glazing. A good proportion of degras is used in the fat liquor.

Combination chrome glacé kid is made from Persians of good quality. The skins are first somewhat heavily stripped with soda, using nearly 1 lb. for every dozen skins, and drumming twenty minutes at 35° C. After washing in two or three changes of warm water they are re-tanned with a basic chrome salt. One lb. of chrome alum is dissolved in 3 quarts water, and made basic by the addition of a solution containing 6 ozs. soda, and the whole made up to 1 gallon; this will be sufficient for a dozen skins. The re-tannage takes place in the drum, and the chrome liquor is added in three portions at quarter-hour intervals, drumming in all for one and a half hour. Salt is added to the drum liquor and also sometimes a coal tar black, or for colours a titanium salt. The goods are then horsed to feed for a day or two, well washed in the drum with water at 50° C., neutralised with 1 per cent. borax on the weight of the wet leather, and again washed until free from borax. They are now struck out and shaved; blue-backing now follows with 4 ozs. acid violet 4 B for each dozen skins. This is done in the polygonal drum with very little water in order to obtain a good penetration of the dye. They are now blacked in the tray just as for glacés (p. 364), washed, and fat-liquored three-quarters of an hour with 1 lb. soft soap and 1 lb. neats-foot oil per dozen skins. They are then horsed up to drain, struck out and dried, hanging up by the hind shanks. They are finished by staking, fluffing, seasoning, and glazing as usual.

For colours the acid dyestuffs are better. The goods after chroming and washing are mordanted with 1 lb. fustic extract and 1 lb. gambier per dozen skins, and then dyed for one hour with 6 ozs. of an acid colour and 6 ozs. sodium bisulphate per dozen skins. They are washed, struck out, lightly fat-liquored with $\frac{1}{2}$ lb. neats-foot oil, $\frac{1}{2}$ lb. soft soap per dozen skins, struck out again and rapidly dried on poles, wet back and dried strained. They are then finished as for coloured chrome glacé as on p. 366.

Semichrome is a name given to a vegetable-tanned upper leather which has been rather more lightly stripped and re-tanned for a few hours with basic chrome salts. Calf skins, kips or split hides may be thus treated, and are usually finished as an imitation box or willow calf, and often sold as such. The goods (*e.g.*, 100 lbs. dry leather) are first stripped of superfluous tan. They are drummed for a short time in water at 35° C., and a solution of $2\frac{1}{2}$ lbs. soda should then be added to the drum, the drumming being continued for about 20 minutes. The goods are next washed thoroughly in the drum with 2 or 3 changes of fresh water at 35° C., until clean. The re-tannage with chrome now takes place. The chrome liquor is made up from 5 lbs. of chrome alum, made basic by the addition of 1 lb. soda in the usual way. The chrome liquor should be added to the goods in a drum in at least three portions and at intervals of $\frac{1}{2}$ to $\frac{3}{4}$ hour. The goods should receive a full hour in the final liquor and are then horsed up overnight. After washing in tepid water they may be neutralised and finished as for box calf; *i.e.*, dyed and fat-liquored, dried, staked, seasoned, glazed, grained, etc. Goods with a poor grain must be printed before the first glazing and grained by hand after the final glazing.

CHAPTER XXVII

THE FINISHING OF FAT AND OIL-TANNED LEATHERS.

Helvetia and crown leathers, on coming from the drum for the last time, are set out on flesh and grain, rinsed through water and set out again. They are then dried somewhat, damped back and curried by coating both flesh and grain with a mixture of cod oil, glycerine, degras and tallow. The goods are then dried further. The superfluous grease is now slicked off and the goods are set out, grained, and dried out.

Chamois for wash leather is not very widely different from crust chamois. After sorting according to quality and size, the skins are staked by hand or by the crutch stake on the perch, and are again sorted. They are next softened and levelled by "grounding" on the perch with the moon-knife, and are worked until quite soft and stretchy. After trimming and sewing up any holes, they are stretched out thoroughly and kept in the stretched condition until the following day.

Chamois for gloving is chosen from the best stout and level skins, which should also be free from cockle. They are first levelled by grounding with the moon-knife on one side only. This may be either the grain or the flesh, whichever is the tightest and best for the finished side. This side is then fluffed on a coarse emery wheel, and afterwards on a fine wheel until a fine velvet surface is obtained. Bleaching now follows, and there are two methods by which this may be satisfactorily brought about.

In the "sun-bleach" the goods are exposed in the open air for several days to the action of sunlight by spreading the skins face up either on the grass[1] or on a tightly-stretched canvas raised 2 to 3 feet from the ground. Before exposure the skins are soaked in an emulsion of soap and oil, using

[1] Hence the term "grass-bleach."

5 lbs. soft soap and 1 lb. cod oil to 30 gallons water. Sometimes soap only is used. The skins are saturated with this liquor, wrung out, and taken direct to the bleaching meadow. This is repeated daily until the skins are quite white, which takes about three days in summer, and up to a fortnight or even more in winter. It will be seen that the process is somewhat tedious, for the skins need constant attention, and have to be taken in at night. A neighbourhood as free as possible from dust and dirt is also essential.

In the other method a "permanganate bleach" is used. In this case the skins must be freed from grease by soaking in a $\frac{3}{4}$ per cent. solution of soda crystals at 30° C., and afterwards drumming half an hour in water at 35° C. until free from alkali. They are now transferred to the permanganate bath, which is a $\frac{1}{8}$ per cent. solution of commercial potassium permanganate to which sulphuric acid one-quarter the weight of the permanganate has been added. For a pack of 30 dozen skins 2 lbs. of permanganate will be sufficient. The goods are paddled or stirred in this solution at 35° C. for about an hour, when they will be evenly dyed with the manganese dioxide formed by the reduction of the permanganate. The skins are now rinsed in clean water and placed in a bath of sulphurous acid, which removes the manganese dioxide and leaves the skins in a bleached condition. The sulphurous acid bath consists of a 3 per cent. solution of liquid sodium bisulphite, and after paddling or drumming the skins in this for twenty minutes, hydrochloric acid one-third the weight of the bisulphite is diluted with an equal volume of water and gradually added to the bath, and the goods are then run until they are quite white, adding more acid if necessary. The skins are now washed well in water at 35° C. About 6 lbs. bisulphite will be sufficient for 30 dozen skins.

"Tucking" follows bleaching. A vat of boiling water containing usually some soft soap is prepared, and each skin in turn is immersed for two to three seconds. The skins shrivel, shrink and curl up, and the area decreases as the substance increases. They are at once taken to dry out in a hot stove at 50—60° C., which fixes the "tuck." The next process is hand staking, by which the skins are pulled out and softened,

and they are then grounded with the moon-knife to raise the nap, and fluffed again on a high-speed emery wheel. The skins are now ready for colouring.

Pigments of mineral origin (ochres, umbers, etc.) may be used for this purpose. The paint may consist of ¼ lb. gum arabic dissolved in 5 gallons water, to which 5 lbs. of ochre are then added. The skins are placed on a horizontal beam with a convex surface covered with lead or tin, and the paint is applied by means of a brush. The goods are now dried out in a hot stove, allowed to cool, staked by hand on the back and "dusted" by beating on a stool until all excess of pigment has been removed. They are now fluffed on the face with a fine emery wheel, and then again coloured, dried, dusted and fluffed.

Dyeing is also done with the coal tar dyestuffs. After tucking the skins are dried, staked fluffed and drummed in a solution of 2 ozs. soda crystals or 3 ozs. soft soap per dozen skins. They are then mordanted for the alizarin colours with chrome alum, using 5 ozs. per dozen skins, and drumming half an hour at 45° C., and then adding the dyestuff and drumming for three-quarters of an hour more to obtain a thorough penetration of the dye. The skins are now struck out and lightly fat-liquored to prevent squeakiness with 2 ozs. egg-yolk per dozen skins. The skins are now dried at 40—50° C., staked, and fluffed on the face side.

The direct dyes are also suitable for dyeing chamois leather without mordants, the Janus, diamine and sulphamine colours being all suitable. With these dyestuffs the operations of tucking, grounding and fluffing are best carried out after dyeing, and the addition of a neutral salt to the dye-bath assists materially in its exhaustion.

The natural dyestuffs may also be used in conjunction with the coal tar colours for dyeing chamois. The skins after bleaching are mordanted with alum, using 1 lb. per dozen skins and drumming for half an hour, and then are dyed with the dyewood extracts and acid dyestuffs. With chrome alum as the mordant, the alizarin colours may be suitably used. A light fat-liquor of egg-yolk is then given, and the skins are afterwards tucked, grounded and fluffed. Occasionally the goods

are mordanted for the coal tar colours by paddling with weak bark liquors.

Buff, buck and formaldehyde leathers are finished by methods similar to those used for chamois, except the last needs no bleaching and that emery wheels entirely replace grounding, etc., for raising the nap on the face.

CHAPTER XXVIII

JAPANNED AND ENAMELLED LEATHERS

JAPANNING consists in applying to the leather successive layers of linseed oil varnishes, which are usually dried by heat. Enamelling is a term applied to precisely the same process, except that the leather is grained or boarded. Japanning is usually done on the flesh or on flesh splits, and enamelling on the grain, but flesh splits are also printed and enamelled. This class of leather is often termed "patent leather," but the writer is unaware that it has ever been made under any patent. The manufacture of the varnishes is largely the trade secret of the japanners, and hence the industry is not progressive. Almost all classes of hides and skins are japanned, but especially split hides for carriage and upholstery leathers, and calf, seal and sheep skins for boot leathers, slippers, dress shoes, ladies' belts, hat leathers, etc.

Any ordinary dressing leather tannage is suitable for japanned hides, but the liming should be somewhat longer in order to kill the grease, and the mellowness of the tannage may be varied according to the degree of softness or firmness desired in the finished goods. The currying is in its earlier stages very similar to other leathers. The goods should be shaved very smooth, and a perfectly level substance obtained, or the enamel will be apt to crack. They should be thoroughly stoned and scoured in order to remove all "stretch," sumached, washed in warm water, slicked out, sammed, lightly buffed on the grain as a rule, thoroughly set out, oiled lightly on the grain with linseed oil and dried out. Any printing is done before the drying out is complete. Mineral oil may be used before drying instead of linseed oil, but the use of tallow, cod oil and any other of the ordinary stuffing greases is to be strictly avoided in this class of leather, as it tends not only to dull the japan but also to cause it to "throw off" or strip

Degras of good quality is, however, employed on the Continent and in America for this purpose. When dry the goods are ready for japanning.

In America many of the large domestic hides are made into this class of leather. They are given usually the "Union" tannage (cp. p. 191), and after about ten days are split in the band-knife machine. A thin "buffing" is first taken off, and

FIG. 107.—Preparing seal skins for enamelling (Messrs. E. & J. Richardson, Newcastle).

afterwards a grain split for carriage coverings, shoe and upholstery leathers; a third split is worked up for cheaper enamels, bag leathers, etc., and a flesh split is left for cheap japans. The splits are re-tanned in handlers, sumached, scoured, lightly stuffed with linseed oil and degras, and dried out on stretching frames, first at ordinary temperature, and then in a steam-heated room with fan ventilation They are then softened—by machine and by boarding—and after sorting are ready for japanning.

All japans have for their basis a good linseed oil, preferably made from Baltic and Belgian seed. This oil contains a considerable proportion of the triglyceride of linolic acid ($C_{17}H_{31}$·COOH), which may be considered as stearic acid in which two pairs of carbon atoms are doubly linked. These double bonds are very susceptible to the action of oxygen, and cause thereby the "drying" of the oil[1] and the production of resinous bodies of unknown constitution. This action has been largely utilised in the manufacture of linoleum. By boiling linseed oil with certain bodies known as "driers" changes occur (not wholly understood, but probably similar to the air-drying process), in which the oil gradually stiffens and is converted into a sort of jelly which dries further into a more or less hard varnish.

The driers are all either oxidising agents or oxygen carriers, and embrace the following substances: Litharge, raw umber, manganese peroxide, borate or "resinate," and Prussian blue (ferric ferrocyanide), the last being the most usual in the production of British japanned leathers as it serves to give also the required black colour.

The nature and extent of the boiling differs for the different coatings, being carried distinctly further for the first coatings in order to obtain a product of such a degree of stiffness that it will not penetrate the leather. The later coatings are not boiled so far, and indeed sometimes without any driers. The driers should be very finely powdered, sieved and thoroughly mixed in with the oil, as should also any pigments for coloured goods. Turpentine, petroleum naphtha and other solvents are used for thinning down the varnishes, and the second is often mixed in at fairly highly temperatures, though much of it evaporates during the addition. The oil is often subjected previous to boiling to a so-called purifying process in which nitric acid is employed to precipitate the impurities and make the japan bright. Rose spirit and other oxidising agents are often used in boiling for a similar purpose. The boiling is done in large cylindrical pans which, to allow for frothing, should not be more than about half full, and which are heated preferably by gas in order to allow an easy regulation of

[1] Theglycerides of other similar acids undergo the same kind of change.

temperature. Large quantities of pungent and combustible vapours are evolved, and the oil should be continuously stirred with a long, perforated iron ladle. The operation lasts less than a day when high temperatures (up to 300° C.) are used, as in many American japanneries, but may extend over several days where lower temperatures are employed. This, however, varies with the nature of the coating and of the drier. The last coatings are often mixed with copal varnish, pyroxylin varnish, etc., and the final layers may consist entirely of such varnishes. The production of japans which dry well in the stove, but which do not give cracky leathers, is a matter of some difficulty, and the use of these final varnishes is of distinct assistance not only in producing a smooth, bright and glossy finish, but in preventing crackiness.

In the application of the japan it is usual in this country to nail down the hides or skins on large boards covered with thick felt cloth and brown paper. These boards slide like drawers into drying stoves, which are unventilated and heated by steam pipes. After several hours' drying the goods receive a first coat of thick japan, which is laid on by means of a serrated slicker and smoothed over by hand. After drying several hours the surface is pumiced, brushed, and a second coat similarly applied, the process being repeated with finer japans and with smooth and thinner slickers until the desired product is obtained. The temperature of the stove may be between 160° and 170° F., but in America this is often exceeded for certain purposes (up to 200° F.), and on the Continent many stoves do not exceed 140° F. In America and on the Continent also the hides or skins are stretched on frames instead of boards, these frames being fitted with screws or toggle joints, which admit any necessary adjustment. In these processes also the goods are often dried in the sun, or put to the sun after stoving. Brushes also are often used instead of slickers for the application of the varnish. No exact statement can be made as to the number of coats of each kind required, as the practice differs so much with different goods and in different works. Smooth japans often receive as many as six or seven coatings, embracing, say, three coatings

of thick ground japan ("daub"), two coatings of thinner japan ("black varnish") and two coatings of finishing varnish. Enamels may receive two coatings only of daub, one coating of "slicker varnish," and two coatings of "enamel varnish" to finish them. Some of the recent productions of japanned chrome calf only receive three coatings altogether. All goods are exposed to ordinary air for a few days after the last stoving, in order to permit moisture from the atmosphere to re-enter the leather. The enamels are then boarded again.

CHAPTER XXIX

THE DRESSING OF WOOL RUGS

The dressing of sheep skins for rugs and mats should perhaps have been dealt with in the chapters on the alum tannages and the finishing of light leathers, but as the methods employed are somewhat unique, it is more convenient to deal with the matter quite separately. The skins as received from the butcher are, of course, first cleansed thoroughly, but as in this case the wool is not to be removed, and indeed is to be of first importance in the finished article, it is necessary to carry this process distinctly further than in the ordinary processes of soaking for depilation, and hence the skins, after being washed in water to remove blood, dung, and loose dirt, and after a preliminary tawing, are thoroughly "scoured" with alkaline soap solutions on both wool and flesh. This removes all dirt and much grease. The next process is to get rid as far as possible of the greasy matters of the skin, which is accomplished usually by stretching the skins taut in special frames and painting the flesh, which is kept upwards, with pastes of whitening (or sometimes fuller's earth) and water. The frames with the skins are then placed in a warm room to dry. The grease is thereby drawn out of the skin into the whitening, which is scraped off when dry. The operation is repeated for very greasy skins. The tanning (sometimes called "tawing" or "dressing") now follows. This is brought about by applying alum and salt to the flesh side. Sometimes the skins are damped down and the salt sprinkled over in the solid state and then well rubbed in by hand, but a common way also is to apply a strong solution of the salts, occasionally assisted by a weak solution of soda. The frames are placed over trestles during this operation, and are then returned to the "stove" to dry out, which process completes the tannage. These various operations are known as "tying in," "degreasing," "trestling off," "stoving," etc.

The skins are now in a condition analogous to the "crust" stage of light leathers, and should be carefully sorted according to their suitability for blacks, whites or colours.

After wetting back the next operation is usually another scouring, to remove more grease from the wool and any dirt obtained in dressing and to prepare the skins for receiving the colouring matter.

The dyeing, which now follows, is one of the most difficult parts of the whole process, for the ordinary methods with the artificial dyestuffs are mostly of no use, and the successful application of the natural dyestuffs generally involves preparatory operations with various re-agents in order to bleach and to render the wool susceptible to the dyestuff and to ensure evenness of colour. The most common of these re-agents is bleaching powder or "chloride of lime," occasionally assisted with ordinary slaked lime. The operation is therefore known as "liming," or "chloring." The bleaching is usually completed by passing the goods through weak solutions of the mineral acids, which also remove lime salts. Where the skins are to be finished white or grey the bleaching is usually with hydrogen peroxide or sulphur dioxide. The dyeing operation may be carried out in one or more vats. In one-vat processes the skins are first immersed in dyewood infusions and then into the same solution after adding the "striker" (see p. 320). The striker may, however, be kept in a separate vat. In those cases where only one or two vats are employed it is usual to ensure evenness of action by drawing the skins through the liquor before immersion, and by handling frequently in the early stages of immersion. An alternative method of working is to have a series of vats of gradually increasing strength and to work the skins through these continuously like a round of handlers (p. 173). This method is cheaper where a good number of skins are being treated, as it permits a greater exhaustion of the dye-bath. Exposure to air and consequent oxidation usually follows dyeing in order to obtain the full intensity of the colour, and then a further scouring with soap and alkali to remove grit and loose colour, to modify the shade, and to give a brightness and gloss to the wool. It will be readily understood also that in the scouring, liming and

dyeing a good proportion of the tannage is lost through the solution of the alum and salt, and that if the skins were simply dried out they would be hard and "tinny." Hence it is an invariable practice to re-tan the goods by tying in the frames again, trestling off with alum and salt liquor, and drying out in the stove. This may also be done after "liming" in order to ensure fast wool. In various stages of the process the goods are passed through weak solutions of sulphuric acid; this is termed "spiriting," and may be used to remove alkali after scouring or liming, to prepare for dyeing, to assist in dyeing, or to modify the shade. In various parts of the process also the goods undergo certain mechanical operations which may be to remove moisture or dye solution (wringing, shaking, mangling, centrifuging, etc.), or to soften the goods when dry (drumming, cageing, etc.). Wool skins should not be laid in pile for any length of time in any stage of manufacture, for they rapidly heat and are soon irreparably ruined. They should be allowed to drain over a "horse" between the different processes.

Blacks, which are the most common and perhaps the most important class, may be dressed by any of the following methods: For high-class work the best skins should be chosen, with the wool at its prime, *i.e.*, 4 to 5 inches long. Curly "Lincolns" (p. 37) are perhaps the most suitable pelts. They are first well washed in water to free from blood and dirt, and well scoured by hand with a solution at 30° C. of ¼ lb. soft soap per gallon of water, to which a little washing soda has been added. The flesh is first scoured and then the wool. The skins are then allowed to soak in the scouring liquor for two hours and re-scoured with a freshly made liquor. After washing as thoroughly as possible to get rid of soap, the skins are ready for degreasing, which for this class of skin should be very thorough. After tanning it is best to "age," the skins for as long as possible, but not less than three months. To wet back they are thrown into water for two hours, and are then carefully scoured to remove all grease. A good plan is to allow the skins to lay overnight and to re-scour them in the morning. They are rinsed through water, then through a weak solution of vitriol, and well

drained. The "liming" now follows, about 120 skins forming a pack. They are placed first into an old chloride of lime liquor for at least two hours, and preferably overnight. A new liquor is now prepared by boiling up 40 lbs. of the bleaching powder and running into a vat with about 500 gallons of water. The skins are drawn through, one by one, and then put down in the liquor for an hour. They are then drawn up and the vat strengthened with 80 lbs. of bleaching powder. The skins are drawn through this continually until the wool is a bright cream colour from tip to root. They are then immersed in the liquor for some time. After drawing up and draining well, they are tied in the frames and trestled off twice. A weak, warm solution of soda is first knifed well over the pelt and the alum and salt liquor then rubbed well in. After standing in the open for two to three hours they are stoved for one hour, and trestled off again and dried out.

To prepare for dyeing they are wet back for two hours in cold water and treated with warm soda solution on the beam to part any locks of dry wool. The skins are then drawn through and afterwards immersed half an hour in weak vitriol, rinsed through two fresh waters and drained two hours. The blacking is by two liquors. The first is the "copperas" striker, being a solution of rusty copperas (6 parts), Roman vitriol (2 parts), verdigris (1 part), and red argol (1 part). The solution is boiled up for three hours after soaking overnight, poured into a vat of water at 35° C., and well stirred up. The skins are drawn through the liquor three times, and then immersed for twelve hours, drawn up and drained. In making the second liquor 1 cwt. of logwood chips and 36 lbs. of fustic chips are boiled till extracted; 12 lbs. of Turkish galls are now roasted, ground, and added to the liquor, which is boiled for an hour and cooled to 35° C. The skins are drawn through weak vitriol, warm water, and after draining, are immersed in this second liquid for an hour, drawn and put down for twelve hours. They are then drawn and hung up in the open air until the colour is fully developed. They are then washed up in cold water and scoured. They are first immersed for a quarter of an hour in 120 gallons of

water with 1 lb. of soda per skin, put through the mangle, scoured with mottled soap and a 13 per cent. soda, 9 per cent. borax solution, at 43° C., and rinsed through warm water. To remove soda and improve the finish they are mangled up in borax and water, then drained, wrung, well shaken, tied in, trestled off, stoved and cooled. This black is called the "copperas black," or "raven black," and retains its colour better than any other. It is a rich, deep, blue-black which, in contrast to many other blacks, improves in appearance each time it is cleaned.

Another method of dyeing blacks is to have a series of six vats with liquor which gradually increases in strength and temperature. To start the system, the liquors are made up as follows:—

Vat.	Logwood extract.	Fustic extract.	Iron nitrate.	Copper acetate.
1	5 lbs.	1 lb.	½ lb.	½ lb.
2	10 ,,	2 lbs.	1 ,,	1 ,,
3	15 ,,	3 ,,	1½ lbs.	1½ lbs.
4	20 ,,	4 ,,	2 ,,	2 ,,
5	30 ,,	5 ,,	3 ,,	3 ,,
6	50 ,,	10 ,,	5 ,,	5 ,,

Packs of twenty-five skins, after dressing and scouring and liming as above, are taken through these liquors, immersing for two hours in each liquor, and finishing up in the strongest liquor at 40° C. For the second pack the weakest vat is emptied, and a new liquor of the same strength as in vat 6 is made up, and the goods therefore go into vat 2, which is now the weakest of the round. On removing from the dye-bath the goods are of a grey colour, and are hung up for three to four hours to drain and oxidise. They are then rinsed in warm water, and the wool is scoured with a warm solution of soft soap, which assists in fully developing the colour and gives a bright gloss. The goods are then trestled off well and stoved out. If it is desired to give more gloss and restore a certain

amount of the natural grease, they may be passed through a fat-liquor of 5 lbs. oil, 5 lbs. soft soap, in 30 gallons water. This is kept at the rather high temperature of 60° C., and the goods drawn through as quickly as possible. They are then drained, dried out, and softened by beating or perching.

Another process for blacking consists in using four vats; the first is a solution of 50 lbs. of logwood extract, the second a solution of 100 lbs. of logwood extract, the third of 3 lbs. of potassium dichromate and the fourth of 6 lbs. of potassium dichromate. After the usual preparations the goods are immersed for one hour in each vat, going first into vat 1, then into vat 3, then into vat 2, and finally into vat 4. The liquors in vats 1 and 3 are now rejected and fresh solutions made up in the empty vats of the same strength as the liquors in vats 2 and 4. These latter liquors being now "used liquors" form the weak liquors for the next pack. The goods are finished off as described for the 6-vat system.

Still another method of producing blacks is by the following 1-vat system. It also differs from the preceding methods in that the liming or "chloring" is omitted, and in consequence the thinnest-woolled skins (Devons, etc.,) may be employed with success. Another consequence of the liming being omitted is that this method of dressing is superior to all others in the wearing qualities of the finished article. The black obtained is very good and cheap to produce, but it has the disadvantage of not being very bright. It is known as the "furrier's black." The dressed skins are scoured well and rinsed through warm water. They are then immersed for two hours or more in a solution at 35° C. of soda, ammonia and oxalic acid, and are put through the mangle to assist in removing grease and dirt from the wool, and then drained for three hours or more. The dye-vat is made up at 35° C. with dark turmeric and logwood extract, thoroughly dissolved and well stirred up. The skins are now rinsed through cold water, placed in the dye-vat wool downwards, and left twelve to eighteen hours. If the skins then "rise," they should be drawn out and the striker added, but if not the vat liquor is again heated up to 35° C. and the skins put back till they do rise. After drawing, the iron liquor and Roman vitriol, together with some sumach and

more logwood extract, are added and the liquor well mixed. The skins are first drawn through, then put down for an hour and then put down for five to six hours. They are now drawn, drained, and hung in the open to oxidise to a deep blue-black. After washing well in cold water they are now scoured with a solution of 12 lbs. borax in 90 gallons water at 38° C. and with a neutral soap. They are rinsed through tepid water and mangled off with a weak, warm solution of boric and sulphuric acids (0·25 per cent. borax, 0·1 per cent. sulphuric acid), wrung, tied in and trestled off twice, and finally caged to soften the pelts and brighten the wool.

Blacking may also be quite effectively done by liming with bleaching powder before the dye-vat is entered, and occasionally the liming is brought about with both stone lime and bleaching powder, but this gives a distinctly poorer result.

Whites can only be satisfactorily dressed with certain good white skins, of which the Leicesters and Lincolns are the favourites. Devons are, of course, of no use. After dressing as usual the skins are wet back in cold water for two hours and thoroughly scoured with hot soda solution and soap. They are then rinsed well in warm water, wrung two to three times in a centrifugal machine, and carefully sorted. This further sorting is desirable because when skins are once bleached with sulphur dioxide they are much more difficult to dye and are always somewhat lustreless. The suitable skins are now taken to the "bleach-house," and, after shaking well to open out the wool, they are hung over poles. This bleach-house is an air-tight chamber with an iron cauldron in the centre in which powdered rock sulphur is burnt. For every four skins 1 lb. of sulphur is taken, and the combustion is started by dropping into the cauldron pieces of hot iron. The room is closed up for twelve hours whilst the bleaching proceeds, and the fumes are then allowed to escape. The skins are now exposed to the open air and again well scoured. They are then bleached in a similar way and re-scoured. After wringing and shaking well they are tied in and trestled off, using a little soda. They are then exposed to the sun and air for as long as possible.

Greys may be dressed by either of two methods. In one

process the skins, after careful selection, are scoured, bleached and re-scoured as for whites and then dyed as follows. For a dozen skins a small vat liquor is prepared by boiling up 8 lbs. of dry logwood chips and running into sufficient water to cover the skins. The skins are drawn through once and 1 lb. of green vitriol dissolved and added to the vat. The skins are now drawn through several times according to the shade required. They are then rinsed through two waters, well scoured with weak soda, rinsed again, tied in and trestled off. Different shades of grey may be obtained by varying the amount of logwood taken.

In the other method the skins are limed and dyed with aniline colours. The chloride of lime is prepared by boiling up 1 lb. per skin and pouring into a vat of cold water. The scoured skins are drawn through three times, put down for an hour, drawn, drained, tied in and dried out. They are next thoroughly wet down, scoured, washed, "spirited off" through weak sulphuric acid, and washed through two waters. They are now ready for dyeing. The dyestuff is dissolved in boiling water and strained through muslin. The dye-vat is filled with water at 37° C., a little of the dye solution added, and the skins are all drawn through once. A little more dyestuff is now poured in and the skins drawn through again, beginning with the last to come out. This is repeated until the desired shade is obtained. As greys invariably dry lighter than they appear when wet, it is desirable to continue the treatment. About a cupful of vitriol is added to the dye liquor, which is then well stirred. The skins are now drawn through continually, if necessary adding more vitriol, and if too dark running off part or all of the liquor and filling up with water. The skins are then wrung, shaken well, tied in and trestled off as usual. Lamb skins are also dressed in grey and are carefully sorted after scouring. They are mangled off with vitriol solution instead of liming and dyed similarly but with less vitriol. They are also given a thorough re-tannage.

Browns are dyed without any liming or other preparation other than scouring. The dye liquor is made up from 100 lbs. terra japonica, 50 lbs. oak bark and 25 lbs. of quercitron bark, which are boiled three to four hours. To this is added a solu-

tion of 30 lbs. dark turmeric, and the liquor well mixed and cooled to 35° C. These quantities are sufficient for fifty skins which are scoured, rinsed and thrown into the liquor till they rise, (about fifteen hours). They are then drawn and allowed to drain into the vat. After throwing off the skins the dye liquor is heated up again to 35° C. and the skins folded in two, wool outwards, and re-inserted into the bath till next day. This is repeated each day till the liquor is exhausted, which will be in about a week. The skins are then mangled, wrung, well shaken, folded, and drawn through a striker of clear saturated lime water, and then put down in the lime liquor for an hour, drawn, and put down overnight. They are then drawn, drained, shaken, and hung out to oxidise as dark as possible. Any unevenness due to grease must be corrected by repeating the lime-water treatment or by going through the whole process again. The skins next are treated with a weak bleaching powder solution to ensure even colour and lustre. They are drawn through, put down for a while, washed in water, drawn through weak vitriol ("spirited off") and again washed. They are scoured at once with soap and soda, rinsed, wrung, shaken, tied in and trestled off. The shade may be "golden brown," "dark brown," etc., according to the amount of acid used in spiriting off. No satisfactory browns can be obtained with the coal tar colours. Bark-tanned sheep skins can also be stained brown by passing through clear lime-water, tying in and trestling off with soda, alum and salt. They are then soaked down, mangled off with weak vitriol ($\frac{1}{8}$ per cent. solution) scoured in weak soda, rinsed and dried out.

Walnuts must be heavily limed as well as heavily dyed to produce satisfactory results, and hence the thickest and heaviest-woolled skins are chosen for this colour. As, moreover, the finish is expensive, good skins also should be taken. The skins are dressed, scoured, and inserted in a fresh liquor of ordinary lime, slaking $1\frac{1}{2}$ cwt. per pack of 120 skins. They are then dried out with the lime in them. After wetting back, washing well, and passing through weak vitriol they are drained and put into a bleaching powder liquor. This is made up with $\frac{1}{2}$ lb. per skin. The skins are drawn through, put down for an hour, drawn, washed well, and spirited off for dyeing.

The dye liquor is made up from 1½ cwt. sandal wood, ¾ cwt. fustic chips, which are boiled well, and to which is added a hot solution of 26 lbs. of dark turmeric. The skins are drawn through, drained one to two hours over the vat, drawn through again, and put in twelve hours or overnight. They are then drawn and drained. The striker is made up by boiling for three to four hours 8 lbs. of roasted and powdered Turkish galls, 4 lbs. red argol, and 4 lbs. verdigris, and adding a pailful of rusty copperas and half a pailful of copper sulphate. When dissolved the liquor is heated to 35° C. The skins are now shaken, drawn through four times, put down two hours, drawn and put down four hours, drawn and hung out to oxidise as fully as possible. They are then washed, drained, and immersed in warm soda solution for about 15 minutes, till a nice brown colour appears, and then mangled off. To get the requisite shade as well as to remove grit the skins are next well scoured with warm soda and soap and then rinsed well through tepid water, wrung, shaken, tied in, and trestled off.

Lamb skins may be dressed in walnut by the same process, using one-third the above quantities. They may also be finished in the following way: They are limed and spirited off like sheep skins and dyed at 35° with a liquor made up from ½ lb. fustic per skin. The skins are drawn through several times and immersed for four hours. They then pass through a striker of ¼ lb. potassium dichromate per skin, and are scoured, rinsed, and finished off as before. This method gives a slightly greener shade than the first. In both processes fustic extract may be substituted for the dyewood.

Crimsons are given the same liming as walnuts, but are tied in and trestled off after coming from the chloride of lime vat. In 2 to 3 days they are soaked well and spirited off for dyeing. To the dye-vat full of water is added a solution of 2 ozs. of turmeric per skin, and the skins immersed half-hour, drawn and put down for four hours. For each skin 1½ ozs. of cerise D. II. (Beck) are dissolved in boiling water and strained into the dye liquor, which is now well plunged. The goods are drawn through, immersed ten minutes and then ten to twelve hours, the temperature being 32° C. After drawing, 4 lbs. vitriol are added to the dye liquor, and the goods are twice

drawn through and drained for two hours. For scouring a solution of 4 lbs. soap and 6 lbs. soda in 90 gallons water is raised to 38° C. and run lightly all over each skin. After rinsing through tepid water the goods are tied in and finished off as usual.

Lamb skins may be similarly treated but with a lighter liming and less dyestuff; a redder crimson may be obtained by adding a little azo-flavine to the dye-bath; a plum colour by adding grey; and a maroon by adding indigo. A lighter crimson may be obtained by giving a lighter liming. An old chloride of lime vat is first entered for one to two hours, and then the goods pass through a new vat made up with 1½ lbs. chloride of lime per skin. The goods are drawn through this three times, put down for fifteen minutes and then for four hours. They are then drawn, drained, tied in and trestled off as above. For Australian and New Zealand pelts it is better to employ less lime and trestle off very thoroughly. Yet another way of dyeing crimsons is to employ varying proportions of Fast Red A and B, and to tie in without scouring.

Blues are also heavily limed and then dyed with indigo. South Downs, Lincoln half-breeds, and other thick-woolled skins are suitable for this dressing. In tying in for trestling these skins should not be stretched very taut, for the heavy liming needs a thicker pelt and closer wool.

The dressed skins are soaked down, mangled off, scoured, and spirited off. The skins are now well trodden in a thin paste of slaked lime in a shallow tank, and, after laying together for an hour, are washed and mangled off with weak vitriol. They are then limed in a new vat with ½ lb. of bleaching powder and ¼ lb. magnesium sulphate per skin. The goods are drawn through once, put down first for ten minutes, then for an hour, drawn, drained, tied in and dried out for at least twenty-four hours. They are next soaked down and mangled off with weak vitriol for dyeing. The indigo is ground and added to sulphuric acid with constant stirring. It is then gradually and carefully heated up to a boil. A vat of water is prepared at 35° C., and a little colour added and stirred up. The skins are drawn through and put down half an hour, more colour added, and the treatment repeated until the desired

shade is obtained. A little vitriol is now added, the skins again drawn through two or three times and, then wrung, tied in and twice trestled off, drying only at moderate heat. Lamb skins may be dyed by the same process, using less lime, much less colour—being easily dyed—and adding no spirit to finish off.

Greens are dressed by precisely the same process as for blues except that picric acid is added to the dye-bath before adding the vitriol. The skins are drawn through until the desired shade has been obtained.

China Sheep Skins are imported to some extent into this country already made up into rugs measuring 6 feet by 2¼ feet. These are re-dressed and dyed in this country. The thin nature of the pelts does not permit them to be limed, so that it is usual to strip the foreign tannage and prepare for dyeing by immersing in a solution of soda, ammonia and oxalic acid. Blacks are dyed in one vat with logwood extract, sumach and iron liquor; walnuts dyed with coal tar colours; greys are bleached and dyed also with aniline colours, like lamb skins; whites and crimsons are treated like sheep skins, except that the latter are not limed. China goats are similarly imported and dressed in black, grey, and crimson.

Angora Goat Skins are dressed often in "china-blue." They are scoured, limed with weak bleaching powder, rinsed and dyed. The dye-bath is made up with a little malachite green, and, after drawing the skins through two or three times, a little methylene blue is added and the skins drawn through again continually until the right shade is reached. They are then wrung and finished off as usual.

Rabbit Skins are dressed with alum and salt and dyed with the Ursol colours after treating with potassium dichromate and other materials. They are finished largely for blacks and sables.

CHAPTER XXX

THE ANALYSIS OF LEATHER

In leather analysis it is first necessary to divide the sample into small pieces. With stuffed leathers and soft leathers this is done by cutting with a sharp knife. With sole and firm leathers the cutting may be supplemented by grinding in the mill used for grinding tanning materials (p. 158). A firm leather may also be clamped in a small vice and shaved with a small plane. This is also a quick and convenient preliminary to grinding in the mill.

Estimation of hide substance.—As leather consists of hide substance coated with and chemically acted upon by tanning matters of various kinds, it will be obvious that the estimation of hide substance in a leather is one of the most important determinations, for by this means the extent of the tannage may be judged in any given sample, the rate of tanning in the yard may be carefully watched, and, as Parker[1] has pointed out, the whole process of the manufacture may be thereby controlled. This determination of the amount of hide substance in a leather is usually brought about by Kjeldahl's method for the determination of nitrogen in organic compounds, the principle of which is that the leather is digested with an excess of concentrated sulphuric acid, which acts both as a dehydrating and an oxidising agent, destroying all carbonaceous matter and converting all nitrogen into ammonium sulphate. The ammonia is then liberated by boiling in the presence of caustic soda, and is collected in a known amount of standard acid, the excess of which is determined by titration with a standard caustic soda solution.

About $\frac{1}{2}$ gm. of leather is weighed into a round-bottomed Jena glass flask of about $\frac{1}{2}$ litre capacity, and 15 to 20 cc. of pure concentrated sulphuric acid is also pipetted into the

[1] Dr. J. G. Parker, J.S.C.I., 1902, p. 839.

flask, which is then heated to boiling in an inclined position in a fume chamber. The sulphuric acid is boiled about half an hour and the leather goes into solution, a clear, colourless liquor being eventually obtained. A small funnel should be placed in the neck of the flask to check evaporation of the sulphuric acid, and if any difficulty is experienced in obtaining a colourless solution the liquor should be cooled somewhat and about 10 gms. pure dry potassium sulphate should be added, and the digestion continued again until a colourless solution is obtained. The solution is now cooled and diluted with distilled water to about 150 cc., and the flask is connected with a tight-fitting cork containing a delivery tap-funnel and a glass tube sloping upwards and connected with the top of a vertical condenser. The lower end of the condenser has attached to it a tube which passes into a flask containing 50 cc. N/10 sulphuric acid. This flask is closed by a rubber bung, through which the tube passes, and through which also is an exit tube filled with pieces of broken glass. In fitting up the apparatus for the experiment, the standard acid is run into the flask through this exit tube, which then acts as a guard tube to prevent any escape of ammonia. The indicator for the titration (two to three drops of a 1 per cent. carminic acid[1] solution) is also added through the guard tube. About 150 cc. of 30 per cent. caustic soda solution are now poured into the tap funnel, and nearly all is

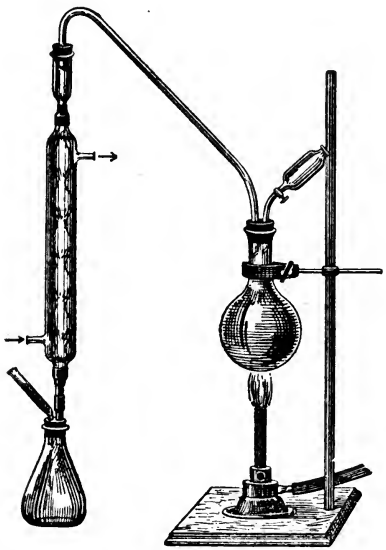


FIG. 108.—Kjeldahl apparatus.

[1] A 1½ per cent. infusion of cochineal is almost equally good, and methyl orange may also be used, but does not give such a sharp colour change.

run into the solution in the Jena flask, which is at once boiled vigorously for fifteen to twenty minutes. The ammonia is absorbed by the standard acid in the receiving flask, and when the distillation is complete this is detached from the condenser, the acid and indicator in the guard tube washed into the solution with distilled water, and the excess acid determined by titration with N/10 caustic soda. Each cc. N/10 sulphuric acid neutralised by the ammonia corresponds to 0·0017 gm. of ammonia, or 0·0014 gm. of nitrogen, or 0·00787 gm. of hide substance.[1]

Another mode of operation, recently suggested by the Author,[2] possesses the advantage that no distillation apparatus is required.

The leather under examination is digested as usual with sulphuric acid until the liquor is clear, and the excess of acid carefully neutralised by adding a solution of caustic soda until a pink colour is obtained with phenol phthalein. A neutral solution of formaldehyde is then added, liberating the sulphuric acid present as ammonium sulphate, according the equation :—

$$2\ (NH_4)_2SO_4 + 6\ H.CHO = 2\ H_2SO_4 + N(CH_2.N : CH_2)_3 + 6\ H_2O.$$

Hexamethylenetetramine, which is formed, is quite neutral to phenol phthalein, and the liberated sulphuric acid is then titrated with N 10 sodium hydroxide solution until the pink colour returns. From the amount of N/10 alkali used, the amount of ammonia originally present as ammonium sulphate, and hence also the amount of nitrogen present in the substance under examination can easily be determined.

The following mode of procedure has been found very convenient. From 0·4 to 0·5 gm. of leather is accurately weighed out into a Jena flask of about 500 cc. capacity and digested over a small flame with 15 cc. of concentrated sulphuric acid until clear. The liquor in the flask is then carefully neutralised to phenol phthalein; a 50 per cent. solution of soda is used until the solution is nearly neutral,

[1] Hide substance contains 17·8 per cent. nitrogen.
[2] Bennett, J.S.C.I., 1909, 291.

and the neutralisation then completed with N/10 sodium hydroxide. The formaldehyde solution (25 cc. of about 40 per cent. strength) is now added to the flask, and after mixing well the liquor is titrated with N/10 caustic soda until a permanent pink is obtained. Each cc. of N/10 alkali required corresponds to 0·0017 gm. of ammonia or 0·0014 gm. of nitrogen, or 0·00786 gm. of hide-substance, as hide-substance contains 17·8 per cent. of nitrogen. Commercial solutions of formaldehyde are usually slightly acid, and of course must be made neutral before adding to the flask. This may be done by neutralising to phenol phthalein with standard caustic soda, or by shaking the solution up with barium carbonate and allowing it to stand overnight.

Estimation of moisture.—Leather has been defined as "dry" in the commercial sense (p. 251) when it does not lose weight on exposure to air at an ordinary temperature and degree of humidity. The amount of moisture present in such air-dry leather is determined by weighing about 5 gms. into a tared porcelain basin and drying at 100—105° C. until it ceases to lose weight. With leathers containing much grease this drying is more easily and more accurately done after the fat extraction.

Estimation of fats.—For this purpose 25 grams of the leather are weighed out and extracted in the Soxhlet apparatus (Fig. 109) with petroleum ether (b.p. under 75° C.) for three to four hours. This apparatus consists of a glass cylindrical vessel fitted with a syphon, which delivers the solvent into a boiling flask. It is also fitted with a side tube, which also passes to the boiling flask. Into the top of the cylinder is fitted a condenser, conveniently of the spherical type. The boiling flask is tared, and, after connection with the apparatus, is heated on the water-bath whilst containing a volume of petroleum ether twice the capacity of the Soxhlet tube. The solvent boils, and the vapour passes through the side tube into the tube of the condenser, from which it falls back on to the leather in the Soxhlet tube. When this is sufficiently full the liquor syphons back again into the boiling flask, taking with it the grease it has dissolved from the leather under examination. After syphoning thus about

ten times the extraction may be considered complete, the solvent is distilled off, and the flask containing the fat residue is dried at 100° C. to constant weight.

It is usual to place a pad of cotton wool (free from fat) at the bottom of the Soxhlet tube to prevent loss of leather in syphoning, and it is necessary to use carbon disulphide in extracting chrome leathers in order that any free sulphur may be completely dissolved and removed with the fats. This sulphur is weighed with the fats, and if necessary determined afterwards by oxidation with nitric acid. The fat-extracted leather residue is dried to constant weight at 100° C. to determine the moisture in the sample. The weight of the dry residue, plus the weight of fats, gives the weight of water by subtraction from 25 grams, the weight of leather taken.

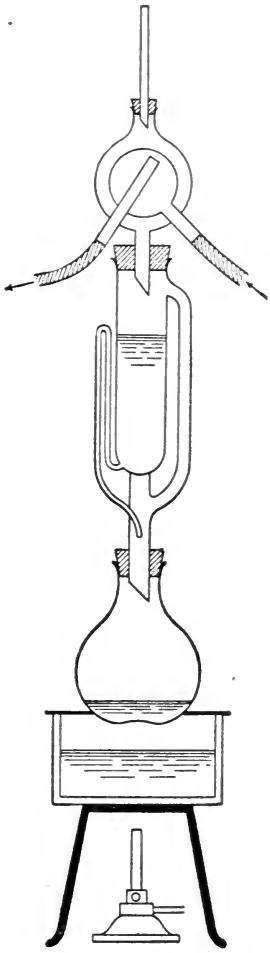


Fig. 109.—Extraction of fat from leather by means of Soxhlet apparatus.

Estimation of water soluble matter.—The dried residue after fat extraction is now extracted further by distilled water, being placed in the Procter extractor (p. 144) and treated just like a vegetable tanning material. The temperature of extraction must not, however, exceed 50° C., and the extraction need not be continued after a colourless and tannin-free percolate begins to come over, which can usually be done within ½ litre. The solution obtained is made up to mark, well mixed and analysed by the hide powder shake method (p. 151), like a vegetable tannin infusion. In this way "total soluble matter," "soluble non-tanning

matter," and by difference "soluble tanning matter," are determined. By making a Kjeldahl determination on a portion of the water-extracted leather it is possible to estimate the proportion of insoluble tanning matter to hide substance. With leathers containing very little grease, *e.g.*, sole and light leathers, the fat extraction may be omitted altogether.

Estimation of glucose.—This is necessary in the case of many sole and heavy leathers, which are often weighted with glucose, and is done by a gravimetric method[1] which depends upon the reduction of an alkaline cupric salt (Fehling's solution) to cuprous oxide, which is filtered off and weighed as metallic copper. The amount of glucose corresponding to the weight of copper obtained is seen from the table given by Koch and Ruhsam given below. In the actual reduction of the Fehling's solution it is quite essential for accuracy to observe most strictly the details specified for carrying out the determination.

The estimation is made from the "water soluble" leather extract obtained in the manner described above. This infusion must contain less than 1 per cent. of glucose, but should contain about 1½ per cent. of total solids. It is first detannised by means of basic lead acetate. The basic lead salt is prepared by heating 300 gms. lead acetate with 100 gms. litharge and about 50 cc. water for some hours on the water-bath, making up to 1 litre and filtering the solution so obtained. A concentrated sodium sulphate solution is now prepared and titrated against 10 cc. of the basic lead acetate until all the lead is thrown down as lead sulphate and no further precipitate is produced. A quantity of the sodium sulphate solution ten times the volume used in this titration is now made up to a litre and used afterwards for removing the excess of basic lead salts. The leather extract is detannised by adding to 200 cc. of it 20 cc. of the lead solution, and after standing a quarter of an hour, filtering off the precipitated lead tannates. The excess of lead salts are now removed by taking 110 cc. of the filtrate (half the total volume of liquid) and adding 10 cc of the sodium sulphate solution, and, after standing a while, filtering off the precipitated lead sulphate.

[1] This method is also applicable to the estimation of glucose in vegetable tanning materials, or as an adulterant in a tanning extract.

Fehling's solution is best kept in two separate solutions, which are only mixed immediately before use. These solutions are made up in the following way :—

(1) 34·639 gms. of pure crystallised copper sulphate are dissolved in distilled water in a $\frac{1}{2}$-litre flask, 10 cc. of N/1 sulphuric acid are added, and the solution made up to 500 cc.

(2) 173 gms. of pure Rochelle salt (crystallised potassium sodium tartrate) and 125 gms. of pure caustic potash are dissolved in distilled water and made up to 500 cc.

In the determination 30 cc. of each of these solutions and 60 cc. distilled water are placed in a 200 cc. beaker and heated to boiling point over a flame. The beaker is now placed in a boiling water-bath and 25 cc. of the detannised and neutral leather extract is added, well mixed, and the mixture maintained at boiling temperature for exactly half an hour. If very little sugar is present the volume of detannised solution taken may be doubled or trebled, but the amount of distilled water must be reduced so as to keep the total volume always at 145 cc.

The precipitate of cuprous oxide is allowed to settle, and at once filtered off through a Gooch crucible and washed well with hot water. It is then dried by washing with alcohol and afterwards with ether, and by placing in the steam oven for about a quarter of an hour. The crucible is now gently ignited in a current of air to destroy any organic matter, and then in a current of hydrogen to reduce the cuprous oxide to metallic copper, in which current it is also allowed to cool. After displacing the hydrogen with air the copper obtained is weighed, and the amount of glucose corresponding is found in the table. As 100 cc. of the original leather extract were diluted to 120 cc. in detannising, the result must be multiplied by 1·2 A leather is not considered to be "adulterated" with glucose unless it contains more than 2 per cent.

Estimation of mineral ash.—A weighed platinum or porcelain basin is heated to redness by a Bunsen burner and about 5 gms. of the leather are weighed out and added to the basin piece by piece as each is incinerated. After adding the last piece the heating is continued at a dull red heat until all organic matter has been burnt away. The basin is then cooled and the mineral ash is weighed.

This ash may be examined either qualitatively or quantitatively by the ordinary methods of inorganic analysis. In the case of chrome leathers the chrome is best estimated by heating the ash with four times its weight of a mixture of equal parts of sodium carbonate and magnesium oxide, stirring frequently with a platinum wire. The chrome salts are then completely converted into sodium chromate. The mixture is dissolved in dilute hydrochloric acid, and the chromic acid estimated by potassium iodide and N/10 thiosulphate, as on p. 236.

The total sulphates and chlorides in chrome leather are best obtained by oxidising the fat-extracted leather with fuming nitric acid, rather than from the ash of air oxidation, or in ignition chromium, aluminium, and iron salts will decompose, and sulphuric acid will be driven off. Ammonium salts are of course also lost in ignition.

Estimation of free mineral acid. — This is exceedingly important in the case of bookbinding and upholstery leathers, for the presence of free sulphuric acid has been shown to be one of the causes of the decay of such leathers. The estimation is best done by the method of Procter and Searle, which is simple, rapid, and fairly accurate. It is carried out as follows :—

"Two to three gms. of the leather are moistened in a platinum basin or crucible with 25 cc. of accurately standardised and measured N/10 sodium carbonate solution, and, after evaporation to dryness, the mixture is charred at a gentle heat till thoroughly carbonised. The carbonaceous mass is pulverised with a glass rod and extracted with boiling water, and the solution filtered through a small ashless filter-paper which is dried and returned to the mass in the crucible, and the whole is ignited till all, or nearly all, carbon has disappeared. The crucible is now cooled, and the ash treated with 25 cc. of N/10 hydrochloric acid to dissolve any calcium carbonate, and the whole is washed into a beaker with the filtrate of the charred mass; methyl orange is added, and if the liquid shows an acid reaction it is titrated with N/10 caustic soda and the amount calculated as sulphuric acid. If the reaction is alkaline, free mineral acid

is absent from the leather, and no notice need be taken of the alkalinity."[1]

The statement of the results of an analysis depends entirely upon the number of determinations that have been made, and this will vary widely with the nature of the leather and the particular point that it is desired to investigate. A complete analysis may be stated as follows:—

Fats.		——	
Moisture.		——	
Water soluble matter	soluble non-tanning matter.	——	(including — per cent. glucose)
	soluble tanning matter.	——	
Leather fibre and insoluble	fixed tanning matter.	——	
	hide substance.	——	
		100·0	

Mineral ash — per cent. (including magnesium sulphate — per cent., sodium sulphate — per cent., etc.).
Free sulphuric acid — per cent.

It will be seldom necessary, however, to go into such detail as this, and modified schemes for stating results can easily be adapted from the above. Broadly speaking, the most important determinations are—for sole leather, hide substance; for curried leathers, grease; for light leathers, free mineral acid; for chrome leathers, chromic oxide and grease. The following analyses may be taken as more or less typical of the class of leather they represent:—

Sole leather, modern mixed tannage.[2]

Hide substance	40·8
Tannin and organic matter	44·7
Mineral ash	0·5
Moisture	14·0
	100·0

Sole leather, West of England tannage.[2]

Hide substance	39·6
Tannin and organic matter	45·5
Mineral ash	1·1
Moisture	14·0
	100·2

Sole leather, oak bark tannage.[2]

Hide substance	47·0
Tannin and organic matter	39·4
Mineral ash	0·6
Moisture	14·0
	101·0

American sole leather.

Fats	1·0
Moisture	15·0
Water soluble (including 8 per cent. glucose and 2 per cent. Epsom salts)	24·0
Leather fibre and insoluble	60·0
	100·0

[1] Procter, "Leather Industries Laboratory Book," 2nd ed., p. 369.
[2] Parker, J.S.C.I., 1902, p. 839.

Belting leather.

Fats	9·5
Moisture	12·0
Water soluble	8·0
Leather fibre and insoluble	70·5
	100·0

Harness leather.

Fats	13·0
Moisture	13·2
Water soluble	20·3
Leather fibre and insoluble	53·5
	100·0

Waxed split.

Fats	38·5
Moisture	9·3
Water soluble	14·2
Leather fibre and insoluble	38·0
	100·0

Willow calf.

Fats	4·4
Moisture	17·6
Mineral ash (including 3·9 per cent. Cr_2O_3)	4·5
Hide substance and organic matter	73·4
	100·0

Glacé kid.

Fats	9·1	(including 0·9 per cent. sulphur).
Moisture	10·5	
Mineral ash	3·7	(including 3·2 per cent. Cr_2O_3).
Hide substance and organic matter	76·7	
	100·0	

TABLE FOR THE DETERMINATION OF THE GLUCOSE IN TANNING MATERIALS FROM THE WEIGHT OF COPPER REDUCED, AFTER HEATING FEHLING'S SOLUTION WITH THE GLUCOSE SOLUTION FOR HALF AN HOUR. (*R. Koch and R. Ruhsam.*)

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
1	0·4	44	18·4	87	40·3	130	62·2	173	83·4
2	0·8	45	18·9	88	40·8	131	62·6	174	83·9
3	1·2	46	19·3	89	41·3	132	63·1	175	84·4
4	1·6	47	19·7	90	41·8	133	63·6	176	84·9
5	2·0	48	20·2	91	42·3	134	64·1	177	85·4
6	2·5	49	20·7	92	42·8	135	64·6	178	85·9
7	2·9	50	21·3	93	43·3	136	65·1	179	86·4
8	3·3	51	21·8	94	43·9	137	65·6	180	86·9
9	3·7	52	22·3	95	44·4	138	66·1	181	87·4
10	4·1	53	22·8	96	44·9	139	66·6	182	87·9
11	4·5	54	23·3	97	45·4	140	67·1	183	88·4
12	4·9	55	23·9	98	45·9	141	67·6	184	88·9
13	5·3	56	24·4	99	46·4	142	68·1	185	89·4
14	5·7	57	24·9	100	46·9	143	68·6	186	89·9
15	6·1	58	25·4	101	47·5	144	69·1	187	90·4
16	6·5	59	25·9	102	48·0	145	69·6	188	90·9
17	7·0	60	26·4	103	48·5	146	70·1	189	91·3
18	7·4	61	26·9	104	49·0	147	70·6	190	91·8
19	7·8	62	27·4	105	49·5	148	71·1	191	92·3
20	8·2	63	28·0	106	50·0	149	71·5	192	92·8
21	8·6	64	28·5	107	50·5	150	72·0	193	93·3
22	9·0	65	29·0	108	51·0	151	72·5	194	93·8
23	9·4	66	29·5	109	51·6	152	73·0	195	94·3
24	9·9	67	30·0	110	52·1	153	73·5	196	94·8
25	10·3	68	30·5	111	52·6	154	74·0	197	95·3
26	10·7	69	31·0	112	53·1	155	74·5	198	95·8
27	11·1	70	31·6	113	53·6	156	75·0	199	96·3
28	11·6	71	32·1	114	54·1	157	75·5	200	96·8
29	12·0	72	32·6	115	54·6	158	76·0	201	97·3
30	12·4	73	33·1	116	55·1	159	76·5	202	97·8
31	12·9	74	33·6	117	55·7	160	77·0	203	98·3
32	13·3	75	34·1	118	56·2	161	77·5	204	98·8
33	13·7	76	34·6	119	56·7	162	78·0	205	99·3
34	14·1	77	35·1	120	57·2	163	78·5	206	99·8
35	14·6	78	35·7	121	57·7	164	79·0	207	100·3
36	15·0	79	36·2	122	58·2	165	79·5	208	100·8
37	15·4	80	36·7	123	58·7	166	80·0	209	101·4
38	15·9	81	37·2	124	59·2	167	80·5	210	101·9
39	16·3	82	37·7	125	59·7	168	81·0	211	102·4
40	16·7	83	38·2	126	60·2	169	81·4	212	102·9
41	17·2	84	38·7	127	60·7	170	81·9	213	103·5
42	17·6	85	39·2	128	61·2	171	82·4	214	104·0
43	18·0	86	39·8	129	61·7	172	82·9	215	104·5

TABLE FOR THE DETERMINATION OF GLUCOSE—*continued.*

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
216	105·0	269	132·7	321	160·3	373	189·4	425	219·6
217	105·5	270	133·2	322	160·9	374	190·0	426	220·2
218	106·0	271	133·7	323	161·4	375	190·6	427	220·8
219	106·6	272	134·2	324	162·0	376	191·1	428	221·4
220	107·1	273	134·7	325	162·5	377	191·7	429	221·9
221	107·6	274	135·3	326	163·0	378	192·3	430	222·5
222	108·1	275	135·8	327	163·6	379	192·8	431	223·1
223	108·7	276	136·3	328	164·1	380	193·4	432	223·7
224	109·2	277	136·8	329	164·7	381	194·0	433	224·4
225	109·7	278	137·4	330	165·2	382	194·6	434	225·1
226	110·2	279	137·9	331	165·8	383	195·2	435	225·8
227	110·7	280	138·4	332	166 3	384	195·7	436	226·4
228	111·2	281	139·0	333	166 9	385	196·3	437	227·1
229	111·8	282	139·5	334	167·4	386	196·9	438	227·8
230	112·3	283	140·0	335	167·9	387	197·5	439	228·5
231	112·8	284	140·5	336	168·4	388	198·0	440	229·1
232	113·3	285	141·1	337	169·0	389	198·6	441	229·8
233	113·8	286	141·6	338	169·5	390	199·2	442	230·5
234	114·4	287	142·1	339	170 1	391	199·8	443	231·2
235	114·9	288	142 6	340	170·6	392	200·3	444	231·8
236	115·4	289	143·2	341	171·2	393	200·9	445	232·5
237	115·9	290	143·7	342	171·7	394	201·5	446	233·2
238	116·4	291	144·2	343	172·2	395	202·1	447	233·9
239	117·0	292	144·7	344	172·8	396	202·7	448	234·5
240	117·5	293	145·3	345	173·3	397	203·3	449	235·2
241	118·0	294	145·8	346	173·9	398	203·8	450	235·9
242	118·5	295	146·3	347	174·5	399	204·4	451	236·6
243	119·0	296	146·9	348	175·0	400	205·0	452	237·2
244	119·5	297	147·4	349	175 6	401	205·6	453	237·9
245	120·1	298	147·9	350	176·2	402	206·2	454	238·6
246	120·6	299	148·4	351	176·8	403	206·8	455	239·3
247	121·1	300	149·0	352	177·3	404	207·3	456	239·9
248	121·6	301	149·5	353	177·9	405	207·9	457	240 6
249	122·1	302	150·1	354	178·5	406	208·5	458	241·3
250	122·7	303	150·6	355	179·1	407	209·1	459	242 0
251	123·2	304	151·1	356	179·6	408	209·7	460	242·6
252	123·7	305	151·7	357	180·2	409	210·3	461	243·3
253	124·2	306	152·2	358	180·8	410	210 8	462	244·0
254	124·8	307	152·8	359	181·4	411	211·4	463	244·7
255	125·3	308	153·3	360	181·9	412	212·0	464	245·3
256	125·8	309	153·9	361	182 5	413	212·6	465	246·0
257	126·3	310	154·4	362	183·1	414	213·2	466	246·7
258	126·9	311	155 0	363	183·7	415	213·8	467	247·4
259	127·5	312	155·5	364	184·2	416	214·4	468	248·0
260	128·0	313	156·0	365	184·8	417	214·9	469	248·7
261	128·5	314	156·5	366	185·4	418	215·5	470	249·4
262	129·0	315	157 1	367	186·0	419	216·1	471	250·1
263	129·5	316	157 6	368	186 5	420	216·7	472	250·8
264	130·1	317	158·1	369	187 1	421	217·3	473	251·4
265	130·6	318	158 7	370	187 7	422	217·9	474	252·1
266	131·1	319	159·2	371	188·3	423	218·4	475	252·8
267	131·6	320	159·8	372	188·8	424	219·0	476	253·5
268	132 2								

INDEX

A.

Acacias, 138
Acid, catechutannic, 121
—— colours, 314
—— ellagic, 117
—— free, in leather, Estimation of, 404
—— gallic, 116
—— gallotannic, 117
—— protocatechuic, 119
—— quebrachotannic, 121
—— quercitannic, 121
Acidity of hide powder, 149
——— of tan liquors, 154
Acids in deliming, 101
Adipose tissue, 9
Albumins, 15
Aleppo galls, 133
Algarobilla, 129
American hides, 35
——— sole leather tanning, 189
——— split hides, tannage of, 198
Ammonia in lime liquors, 65
Angora goats for rugs, 396
Antiseptics, 25
Archbutt & Deeley process for softening water, 43
Army grains, currying, 304
—— uppers, tannage of hides for, 198
Arrector, 7
Arsenic, sulphide, 63
Astringent tannins, 169

Bacilli, 23
Bacteria, 22
Bacterial action in soaking, 50
Bag hides, currying, 308
—— —— tannage of, 202
—— tannage of goat skins, 204
Band knife splitting machine, 281
Bark, birch, 139
—— hemlock, 136
—— larch, 139
—— mallet, 139
—— mangrove, 137
—— mimosa, 137
—— oak, 133
—— pine, 139
—— willow, 132
Barkometer, 155
Basic colours, 312
Basils, deliming sheep skins for, 107
—— for linings, etc., 348
—— tannage of, 208
Bate-burns, 97
—— shaving, 92
Bating, 97
Beaumé degrees, 156
Belt knife splitting machine, 281
Belting leather, finishing chrome, 369
——— ——— tannage of, 194
——— ——— ——— of chrome 235
——— ——— unhairing hides for, 83

Bends, 32
——— cutting, 266
Berkefeld filter candle, 146
Bettering method of liming, 78
Birch bark, 139
Black harness dressing, 297
—— wool rugs, 387
Blast system, 255
Bleaching, 320
———— chamois, 377
———— hemlock sides, 269
Bleeding, 216
Block gambier, 134
Bloom, 117
Bloomed butts, finishing, 268
———— —— liming hides for, 81
Bookbinding calf, tannage of, 207
Boric acid in deliming, 100
Bottle tannage of goat skins, 204
Box calf, deliming for, 105
— — finishing, 360
— — tannage of, 227
— — unhairing skins for, 84
— sides, tannage of, 227
Brazilwood, 319
Bridle leather, currying, 308
——— ——— tannage of, 202
Brined hides, 28
British hides, 33
Brown harness dressing, 300
Brush dyeing, 329
Brushing heavy leather, 266
———— light leather, 343
Buck leather, tannage of, 249
Buff leather, tannage of, 248
Buffalo hides, 36
——— method of liming, 81
Buffing, 275
Burning in, 292
Butts, 32

C.

Calcium sulphydrate, 63
Calf for box, finishing, 360
—— k d, deiiming for, 106
Calf kid, finishing, 373
—— — liming skins for, 84
—— — tannage of calf skins for, 242
—— tannage of heavy, 201
—— ——— of shoe, 201
·-·- willow, finishing, 363
Calf skins, deliming, 105
———— for alum tannage, liming of, 84
———— for bookbinding, lining of, 84
———— for bootwork, lining of, 84
———— for calf kid, tannage of, 242
———— for chrome, liming of, 84
———— for light leathers, tannage of, 207
Canaigre, 139
Candle, Berkefeld filter, 146
Cape Sumach, 139
Catechins, 120
Catechol, 119
———— tanning materials, 133
———— tannins, 119
Catechutannic acid, 121
Caustic soda in liming, 64
——— —— in soaks, 53
——— —— process for water softening, 43
Cell, 6, 19
Centrifugal fan ventilation, 255
Chamois, chrome, 233
———— finishing chrome, 367
———— leather, tannage of, 247
Chemical assistance in soaking, 52
———— control of chrome tannages, 236
———— ——— of lime-yard, 90
———— ——— of tan yard, 140
———— deliming agents, 100
Chestnut extract, 132
Chloring wool rugs, 386
Chrome alum liquor, basic, 223
——— belting, finishing, 369

Chrome belting leather, tannage of, 235
——— calf, deliming for, 105
——— —— tannage of, 227
——— chamois, finishing, 367
——— ——— tannage of, 233
——— extracts, 224
——— glacé, finishing, 365
——— harness, finishing, 368
——— ——— tannage of, 235
——— leather, general qualities of, 225
——— ——— history of, 210
——— liquors, 223
——— motor butts, finishing, 369
——— picking bands, finishing, 368
——— ——— —— tannage of, 234
——— sole leather, finishing, 369
——— — ——— tannage of, 235
——— tannage by one-bath process, 219
——— ——— — two-bath process, 213
——— ——— nature of, 211
Chroming bath, 213
Clark process for softening water, 42
Clearing, 332
Coal tar colours, 312
Cochineal, 319
Cockle, 110
Cold-sweat system, 57
Colour measurement in tanning materials, 154
——— shades, 321
Coloured glacé, finishing, 365
Colours, coal tar, 312
——— primary, 321
Colt, 110
Combination chrome glacé, finishing, 374
Combined one-bath two-bath chrome tannage, 229
Commercial dye-stuffs, 316
Complementary colours, 322
Connective tissue, 8
Continental hides, 35
Coriaria myrtifolia, 131
Corium, 8
Crown leather, 246
Crushing myrobalans, 158
Cube gambier, 134
Curing hides, 27
——— —— by drying, 27
——— —— by drysalting, 29
——— —— by salting, 28
Currying Army grains, 304
——— bag hides, 308
——— bridle leather, 308
——— glove hide bellies, 307
——— of harness leather, 297
——— legging leathers, 310
——— levant, 307
——— lining leather, 308
——— memel butts, 306
——— picking band butts, 310
——— satin leather, 304
——— strap butts, 295
——— waxed calf, 303
——— —— kip butts, 301
——— —— shoe butts, 304
——— —— splits, 303
Cutch, 138, 319
Cutis, 8

Deer Skins, 40
Degras, 248
Degreasing sheep skins, 107
Deliming calf skins, 105
——— dressing hides, 104
——— E. I. kips, 105
——— goat skins for chrome glacé, 111
——— ——— for moroccos, 111
——— harness backs, 103
——— lamb and kid skins for glove kid, 111

Deliming seal skins, 112
——— sheep skins for basils, 107
——— ——— for chrome glacé, 108
——— ——— for roans, 107
——— ——— for roller leather, 107
——— skivers, 107
——— sole butts, 102
——— strap butts, 103
——— with acids, 100
Depickling, 109
Depilation by liming, 58
——— by sweating, 57
Detannisation, 147
Digallic acid, 117
Direct cotton dyes, 315
Disinfectants, 25
Disintegrator, 158
Dissolved hide substance in limes, 90
Divi-divi, 129
Dog dung, use of, 95
Dongola goat, finishing, 373
——— Tannage of goat skins for, 243
Downward ventilation, 255
Drawn grain, 100, 169
Drench acids, 99
Drenching, 98
Dressing hides, deliming, 104
——— —— tannage of, 197
——— —— unhairing, 84
——— leather liquors, 199
Drum method of dyeing, 328
—— oiling, 268
—— scouring, 266
—— stuffing, 288
—— tannage of sole leather, 192
—— tanned sole leather, finishing, 271
—— ——— — ——— liming hides for, 81
—— tanning, principles of, 178
Drums in soaking hides, 52
Dry leather, definition of, 251
Drying hides, 27
——— residues in tannin analysis 149
Drysalting hides, 29
Dull calf, 362
—— dongola, finishing, 374
—— kid, finishing, 365
Dusters, 172
Dyeing, methods of, 324
——— theory of, 330
——— to shade, 324
Dye-stuffs, artificial, 312
——— commercial, 316
——— natural, 317

E.

E. I. goat and sheep, finishing, 351
— —— skins, 40
— kips, 36
— —— deliming, 105
— —— tannage of, 200
— —— unhairing, 84
Elastic fibres, 8
Ellagic acid, 117
Ellagitannic acid, 110
Enamelling, 380
Enzymes, 20
Epidermis of skin, 6
Erector pili, 7
Erodin, 97
Estimation of hide substance, 397
Evaporation in tannin analysis, 149
Extract, chestnut, 132
——— manufacture, 164
——— oakwood, 132
——— quebracho, 135
Extraction for analysis of tanning materials, 144
Extracts, chrome, 224
——— solubilised, 135

F.

Fan ventilation, 254
Fat glands, 8
— liquoring, 356
— tanned leathers, 246
Fats in leather, Estimation of, 400
Fellmonger, 37
Fellmongering, 85
———— with sulphide and lime, 87
Fermentive bates, 98
Ferments, organised, 21
———— unorganised, 20
Fibres elastic, 8
Filter bell, 147
Filtration for tannin analysis, 145
Finishing basils, 348
———— box calf, 360
———— buff, buck and formaldehyde leathers, 379
———— calf kid, 373
———— chamois for wash leather, 376
———— chrome chamois, 367
———— ———— belting, 369
———— ———— glacé, 365
———— ———— harness, 368
———— ———— motor butts, 369
———— ———— picking bands, 368
———— ———— sole leather, 369
———— combination chrome glacé, 374
———— dongola goat, 373
———— drum tanned sole leather, 271
———— E. I. goat and sheep, 351
———— glacé kid, 364
———— glove kid, 371
———— goat moroccos, 344
———— heavy chrome butts, 362
———— Helvetia and crown leathers, 376
———— hemlock sides, 269
———— oak-bark sole leather, 269
Finishing roans, 350
———— roller leather, 350
———— scoured bends, 259
———— seal moroccos, 346
———— semichrome, 375
———— sheep skins for glacé, 365
———— skivers, 349
———— willow calf, 363
Fishings, 160
Flagellæ, 23
Flavones, 121
Fleshing machines, 73
Flint hides, 27
Floaters, 172
Fluffing, 343
Formaldehyde leather, 250
Fungi, 21
Fustic, 318

G.

Gallic acid, 116
Gallotannic acid, 117
Galls, Turkish, 133
Gambier, 134
Gelatin, 16
Glacé calf, 362
—— Deliming goat skins for chrome, 111
—— ———— sheep skins for chrome, 108
—— kid, finishing, 364
—— — tannage of goat skins for chrome, 230
—— — unhairing goat skins for, 89
—— sheep, finishing, 366
—— Tannage of sheep skins for chrome, 110
Glands, fat, 8
———— sebaceous, 8
———— sweat, 9
Glassing, 342
Glassy layer, 9
Glazing, 341

Glove hide bellies, currying, 307
—— kid, Deliming lamb and kid skins for, 111
—— — Finishing, 371
—— — Tannage of lamb and kid skins for, 241
—— — Unhairing kid and lamb skins for, 88
Glucose chrome tanning liquor, 224
—— in leather, Estimation of, 402
Glue, 18
Goat skins, 39
—— —— for chrome glacé, deliming, 111
—— —— for glacé and dull kid, tannage of, 230
—— —— for glazed dongola, tannage of, 243
—— —— for moroccos, deliming, 111
—— —— — —— tannage of, 204
—— —— liming of, 89
—— —— unhairing of, 89
Grain of leather, 9
Graining, 336
Gravimetric estimation of tannin, 142
Grinding tanning materials, 157

H.

Hair papilla, 7
Hand shaving, 275
—— stuffing, 288
Handlers, 172
—— how to work a round of, 173
Hard grain morocco, 344
Hardness, magnesia, 45
—— of water, 41
—— permanent, 42, 44
—— temporary, 42, 44
Harness backs, Deliming, 103
—— finishing chrome, 368
Harness leather, currying of, 297
—— —— tannage of, 195
—— —— —— of chrome, 235
—— —— unhairing hides for, 83
Heavy chrome butts, finishing, 362
Helvetia leather, 246
—— and crown leathers, finishing, 376
Hemlock bark, 136
—— tannage of American sole leather, 189
—— sides, finishing, 269
Hen dung, use of, 97
Hide splits, dressing, 354
—— substance, estimation of, 397
Hides, 27
—— American, 35
—— British, 33
—— Continental, 35
—— Irish, 34
—— for dressing leather, tannage of, 197
—— for sole leather, tannage of 179
—— selection of, 29
Hippopotamus hides, 36
Hook drying, 263
Horny layer of skin, 6
Horse hides, 36
Humidity of atmosphere, 251
Hyaline layer, 9
Hypo bath, 216
—— dip, 219

I.

Imitation glacé, finishing, 366
Increase in tannin strength in liquors, 168
Indigo, 319
Infusion for tannin analysis, making the, 143

Interfibrillar substance, 8
Irish hides, 34
Iron liquor, 320

J.

Jacking, 281
Japanning, 380

K.

Keratins, 15
Kid and lamb skins, unhairing of, 88
— skins, 40
— —— for glove kid, deliming, 111
— —— — —— — tannage of, 241
Kip bellies for straps, currying, 310
Kips, 29, 36
Knoppern, 133

L.

Lactic acid in deliming, 100
Lamb skins, 39
—— —— for glove kid, deliming, 111
—— —— — —— — tannage of, 241
Larch bark, 139
Layer, glassy, 9
—— hyaline, 9
Layers, 176
Leaching under pressure, 164
——— 160
Leather, definition of, 3
Legging leathers, currying, 310
—— ——— tannage of, 200
Lentisco, 131
Levant dressing, 307
——— morocco, 315
Lime on skin, action of, 61
—— required for softening water, 45
—— speck, 110
Liming, basils, 348
——— depilation by, 58
——— dressing hides, 84
——— E. I. kips, 84
——— goat skins, 89
——— hides for sole leather, 80
——— kid and lamb skins, 88
——— leather, currying, 308
——— of calf skins, 84
——— seal skins, 90
——— sheep skins, 86
——— wool rugs, 386
Liquor, basic chrome alum, 223
——— glucose chrome tanning, 224
——— packs, 176
Liquors, chrome, 223
——— for dressing leather, how to work, 199
——— of sole leather yard, how to work, 188
Logwood, 317
Löwenthal method of tannin analysis, 140

M.

Machine shaving, 277
Magnesia hardness, 45
Mallet bark, 138
Mangrove bark, 137
Mechanical treatment in soaking, 50
Mellow lime liquors, 65
——— limes, 65
——— tan liquors, 169
Memel butts, currying, 306
Micrococci, 23
Microscopic examination of skin, 9
——— ——— of sumach, 130

Mimosa bark, 137
Mineral acid in leather, Estimation of, 404
——— ash in leather, Estimation of, 403
——— tannage, nature of, 211
Mixed tannage of sole leather, 183
Moellon, 248
Moisture in leather, Estimation of, 400
Mordants, 319
Morocco finishing, hard grain, 344
—— —— levant, 345
Moroccos, deliming goat skins for, 111
——— tannage of goat skins for, 204
——— unhairing goat skins for, 89
Motor butts, 235
—— —— finishing chrome, 369
Moulds, 22
Myrobalans, 126

N.

Neutralisation, 355
Nucleus, 19

O.

Oak bark, 133
— —— sole leather, finishing, 269
— —— —— —— liming hides, 81
— —— tannage of sole leather, 179
— tannage of American sole leather, 189
Oakwood extract, 132
Offal, finishing sole, 267
Official method of tannin analysis, 151
One-bath process of chrome tanning, 219
One-pit system of liming, 78
Orchil, 319
Organised ferments, 21

P

Packer hides, 28
Paddle method of dyeing, 327
Paddling to start tanning, 171
Pars papillaris, 8
Pelt test, 154
Perching, 358
Permanent hardness, 42, 44
Phlobaphenes, 121
Phloroglucol, 120
Picking band butts, chrome, 234
——— —— —— currying, 310
——— —— —— vegetable tannage of, 203
——— bands, finishing chrome, 368
Pickling, 109
Pig skins, 40
Pigeon dung, use of, 97
Pin, 263
Pine bark, 139
Pinholes, 110
Pipy grain, 100
Pistacia, 131
Pitted, 110
Plumping, 61
Pole drying, 263
Porpoise skins, 40
Porter-Clark process for softening water, 42
Press leach system, 162
Primary colours, 321
Principles of alum tannages, 239
——— of deliming, 92
——— of fat tannages, 245
——— of liming, 65
Procter-Bennett shake method of tannin analysis, 148

Procter's filter bell, 147
——— glucose chrome tanning liquor, 224
Proteids, 10
Protocatechuic acid, 119
Protoplasm, 19
Puered goods, condition of, 95
Puering, 94
Pullman-Payne process of liming, 79
Putrefaction, 24
Putrid soaks, 50
Pyrogallol, 116
——— tanning materials, 124
——— tannins, 116

Q.

Qualities of chrome leather, 226
Quantities for analysis, 145
Quebracho, 135
Quebrachotannic acid, 121
Quercitannic acid, 121
Quick unhairing of hides for sole leather, 82

R.

Rabbit skins, 396
Reds, 121
Redwoods, 319
Rete Malpighi of skin, 6
Roans, deliming sheep skins for, 107
——— finishing, 350
——— tannage of, 208
Rockers, 171
Roller leather, deliming sheep skins for, 107
——— ——— finishing, 350
——— ——— tannage of, 208
Rolling, 343
——— "on" sole leather, 263
——— "off" sole leather, 265
Round of handlers, how to work a, 173
Rounding hides, 32

S.

Salting hides, 28
Samming, 256
Sampling tanning materials for analysis, 142
Satin leather, currying, 304
Schultz process, 213
Scoured bends, finishing, 259
——— ——— liming hides for, 80
Scouring dressing leather, 282
——— sole leather, 260
Screw fan ventilation, 254
Scudding, 93
Seal morocco, finishing, 346
Seal skins, 40
——— deliming, 112
——— tannage of, 206
——— unhairing of, 90
Seasoning, 340
Sebaceous glands, 8
Selection of hides, 29
Selective action of enzymes, 20
Semichrome, finishing, 375
Seymour-Jones on pickling, 110
Shake method, 148
Sharpening limes, 64
Shaving, 274
Shearlings, 87
Shed work for sole leather, 262
Sheep skins, 36
——— chrome tannage of, 232
——— degreasing, 107
——— fellmongering of, 85
——— for basils, deliming 107
——— for chrome glacé, deliming, 108
——— for roans, deliming, 107

Sheep skins for roller leather, deliming, 107
——— for skivers, deliming, 107
——— splits for chrome chamois, 233
——— splitting, 107
——— tannage of, 208
Shoe calf, tannage of, 201
Short liming for sole leather, 82
Skin, epidermis of, 6
—— horny layer of, 6
—— its chemical composition, 10
—— its physical structure, 6
—— microscopic examination of, 9
—— rete Malpighi of, 6
Skins, 36
Skivers, deliming, 107
——— paste grain, etc., 349
——— tannage of, 208
Skiving, 281
Slippy hides, 30
Slugger, 267
Soaking calf skins, 55
——— chemical control of, 56
——— dried hides, 55
——— dry-salted hides, 55
——— E. I. kips, 55
——— for shaving, 274
——— goat skins, 55
——— market hides, 54
——— salted hides, 54
——— seal skins, 56
Society of Arts, report of committee of, 109
Sod oil, 248
Sodium sulphide for depilation, 62
——— ——— in soaks, 53
Softening water, 42
Sole butts, deliming, 102
— leather, American tannage, 189
— ——— chrome tannage of, 235
— ——— drum tannage of, 192
— ——— finishing chrome, 369
— ——— ——— drum tanned, 271
Sole leather, finishing mixed tanned, 259
— ——— ——— oak bark, 269
— ——— ——— West of England tannage, 268
— ——— liming hides for, 80
— ——— liquors, how to work, 188
— ——— modern mixed tannage of, 183
— ——— oak bark, tannage of, 179
— ——— tannages, 179
— ——— West of England tannage of, 181
Sour tan liquors, 171
Souring, 332
Speck, lime, 110
Spirilla, 23
Split hides, tannage of American 198
Splits, currying of waxed, 303
—— sheep skins, tannage of, 233
Splitting, 277
——— sheep skins, 107
Sprinkler leaches, 164
Spueing of curried leathers, 293
Staining, 329
Staking, 358
Staling, 85
Stocks in soaking hides, 51
Stoning, 281
Stove drying, 256
Strap butts, currying of, 295
—— —— deliming, 103
—— —— finishing chrome, 369
—— —— tannage of, 194
Straps, currying kip bellies for, 310
Striking out light leathers, 333
——— — sole leather, 263
Stripping, 332
Stuffing, 285
Substance Interfibrillar, 8
Sulphide of sodium, 62
Sumach, 129

Sumach calf, deliming, 105
——— ——— liming skins for, 84
——— Microscopic examination of, 130
Sumaching dressing leather, 285
Suspenders, 171
Suspension system of liming, 80
Sweat glands, 9
Sweating, depilation by, 57
sheep skins, 85
Sweet tan liquors, 171
Swelling with lime, 61

T.

Tainting stoves, 85
Tamerix, 131
Tannage, by one-bath chrome process, 219
——— of American sole leather, 189
——— — ——— ——— split hides, 198
——— — bag, portmanteau, and bridle leather, 202
——— — basils, 208
——— — belting leather, 194
——— — box calf, willow calf, box sides, 227
——— — buck leather, 249
——— — buff leather, 248
——— — calf skins for calf kid, 242
——— — ——— for light leathers, 207
——— — chamois leather, 247
——— — chrome belting, 235
——— — ——— harness, 235
——— — crown and Helvetia leather, 246
——— — dressing hides, 197
——— — E. I. kips, 200
——— — goat skins for glacé kid, 250
Tannage of goat skins for glazed dongola, 243
——— — ——— for moroccos, 204
——— — harness leather, 195
——— — heavy calf, 201
——— — hides for Army uppers, 198
——— — lamb and kid skins for glove kid, 241
——— — legging leather, 200
——— — motor butts, 235
——— — picking band butts, 203
——— — ——— ——— butts, chrome, 234
——— — roans, 208
——— — roller leather, 208
——— — seal skins, 206
——— — sheep skins, 208
——— — ——— for chrome glacé, 233
——— — "shoe calf," 201
——— — skivers, 208
——— — sole butts, chrome, 235
——— — — leather in drum, 192
——— — — ——— mixed, 183
——— — — ——— oak bark, 179
——— — — ——— West of England, 181
——— with two-bath process, 213
Tannin analysis, indirect Gravimetric method of, 142
——— ——— Löwenthal method of, 140
——— definition of, 113
——— sources of, 123
Tannins, catechol, 119
——— classification of, 115

Tannins, methods of purification of, 114
——— pyrogallol, 116
Temporary hardness, 42, 44
Texture of hide powder, 149
Three paddle tannage for goat skins, 204
—— pit system of liming, 75
Tintometer, 154
Tissue, adipose, 9
Topping, 315
Tray method of dyeing, 324
Turkish galls, 133
Turret drying, 255
Twaddel degrees, 156
Two-bath process of chrome tannage, 213

U.

Unhairing, 68
——— dressing hides, 84
——— E. I. kips, 84
——— goat skins, 89
——— hides for belting leather, 83
——— ———harness leather, 83
——— kid and lamb skins, 88
——— machines, 69
——— seal skins, 90
——— sheep skins, 85
Union splitter, 279
—— tannage of American sole leather, 191
Unorganised ferments, 20
Unwoolling sheep skins, 85
Upper leather, deliming hides for, 104
—— ——— liming hides for, 84
—— ——— tannage of hides for, 197

V

Valonia, 124
Vatting sole leather, 261
Vegetable calf, deliming for, 105
Vibrating knife splitting machine, 279
Volumetric estimation of tannin, 140

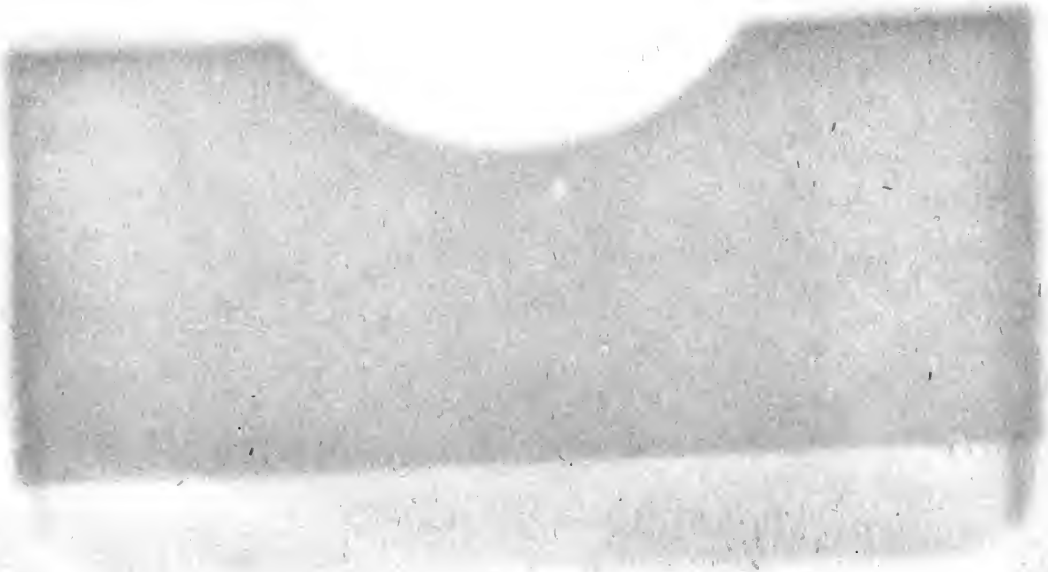
W.

Walrus hides, 36
Warbles, 30
Warm sweat system, 58
Water soluble matter in leather, estimation, 401
Wattle, 138
Waxed calf, currying, 303
——— kip butts, currying, 301
——— shoe butts, currying, 304
——— splits, currying of, 303
Weather drying, 253
Weighting hemlock sides, 269
West of England tannage of sole leather, 181
Wet and dry bulb thermometer, 252
White wool rugs, 391
Whitening, 277
Willow bark, 132
——— calf, finishing, 363
——— ——— tannage of, 227
——— ——— unhairing skins for, 84
Wood,—action of puer, 96
Wool rugs, dressing, 385
Working of drench, 100

Y.

Yar-yan evaporator, 165
Yeasts, 21

THE WHITEFRIARS PRESS, LTD., LONDON AND TONBRIDGE.



of Toronto
ıbrary

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

Acme Library Card Pocket
Under Pat. "Ref. Index File"
Made by LIBRARY BUREAU